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(54) **Title:** GRAPHENE BASED SCREEN-PRINTABLE INK AND ITS USE IN SUPERCAPACITORS

(57) **Abstract:** A screen-printable ink comprising (a) nano graphene platelets, (b) a polymer comprising aniline monomeric units, (c) at least one solvent.

Graphene based screen-printable ink and its use in supercapacitors

The invention relates to a graphene based printable ink, an electrode comprising such inks and a supercapacitor comprising such electrode.

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Background of the Invention

Supercapacitors store energy using either ion adsorption (electrochemical double layer capacitors) or fast surface redox reactions (pseudo-capacitors). It is an important energy-storage device due to their high power density, reversibility, long cycle life. Graphene is an ideal electrode material for supercapacitors due to its high conductivity, high surface area, and good mechanical properties. Graphene electrodes can store energy using ion adsorption.

A general summary of the application of graphene based materials in superacapacitors can be found in small 2012, 8, No. 12, 1805–1834.

In Advanced Materials 2011, 23 (33), 3751-3769 polyaniline (PAni) has been considered as promising electrode material due to its high pseudocapacitance.

Chemistry of Materials 2010, 22 (4), 1392-1401 discloses composite materials based on graphene and polyanilines that have been tested as supercapacitor electrodes and high capacitances and stability have been achieved due to the synergetic combination of the excellent conducting and mechanical properties of graphene and high pseudocapacitance of the polyanilines. Supercapacitor devices based on graphene/polyaniline show large electrochemical capacitance 210~480 F/g. However, such composite materials are difficult to apply on substrates and therefore difficult to integrate into electronic manufacturing processes.

ACS Nano Vol. 6, No. 2, 1715–1723, 2012 discloses polyaniline-grafted reduced graphene oxide for producing electrochemical supercapacitors.

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Langmuir 2012, 28, 12637–12646 discloses a layer-by-layer self-assembled multilayer desposition of graphene oxide and polyaniline. The graphene oxide in the layers is then reduced to graphene to receive a graphene/polyaniline multilayer structure. Its application in supercapacitors was assessed.

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ACS Nano Vol. 3, No. 7, 1745–1752, 2009 discloses the preparation of a graphene/polyaniline composite paper by in situ anodic electropolymerization of aniline monomers into a PAni film on graphene paper.

ACS Nano 2010, 4 (4), 1963-1970 discloses a method for preparing stable aqueous dispersions of chemically converted graphene ("CCG")/polyaniline-nanofiber composites. The dispersion was prepared by mixing the purified polyaniline-nanofiber dispersion with a controlled amount of CCG colloid at pH 10 under sonication. The dispersion was then filtrated to receive the

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graphene/PANI composite film. Due to the low concentrations (low viscosity) of the CCG/polyaniline dispersion the composition cannot be screen printed.

5 Nanoscale 2010, 2, 2164-2170 discloses a graphene/polyaniline hybrid material for supercapacitors.

10 US 2012/0028127 A1 discloses a graphene based ink for forming electrodes of printable batteries or supercapacitors. The ink comprises titanium dioxide and a binder. The binder may be selected from polyaniline.

15 US 2010/0239871 A1 discloses polysiloxane inks which contain a pigment, a radical polymerization initiator and optionally an electrically conductive polymers like polyaniline. Graphene sheets may be used as the pigment.

20 Printed electronics is a technology aimed at unconventional electronic device manufacture on plastic/paper foils by printing techniques. In view of industry technology, screen printing technology is promising because it enables the large-scale production of low-cost, reproducible thin film electrode. However, formulating printable inks comprising nano graphene platelets (NGPs) and Polyaniline to fabricate a screen-printable supercapacitor electrode has never been explored until now.

25 For the conventional supercapacitor device fabrication, the electrode materials are coated on Pt or Al foils, Pt or Al foils are used as current collectors. The metal current collectors are expensive and heavy.

30 Therefore it is an object of the present invention to provide inexpensive, flexible, light-weight and environmentally friendly energy storage devices. In particular, it is an object of the present invention to provide fully printable charge storage devices for allowing full integration into the manufacturing process of electronics. It is a further object of the invention to provide an ink, which can be prepared from standard materials available on the market in ton scale using a simplified preparation process. It is a yet another object of the invention to provide a facile one-pot process for preparing a screen-printable ink.

35 Summary of the Invention

A first embodiment of the present invention provides a screen printable ink comprising

- (a) nano graphene platelets,
- (b) a polymer comprising aniline monomeric units,
- (c) at least one solvent.

40 It was surprisingly found that such graphene based inks can be screen printed on a conductive substrate and that the received thin film can be used directly as a supercapacitor electrode. By

using such ink inexpensive, flexible, light-weight and environmentally friendly energy storage devices can be manufactured.

5 Furthermore, the film fabrication speed can be enhanced to realize very short timescales of just about 0.1 seconds.

A further embodiment of the present invention provides an electrode comprising a printable ink as defined herein.

10 Yet another embodiment of the present invention provides a process for preparing an electrode comprising:

- (i) providing a printable ink as described herein,
- (ii) providing a substrate,
- 15 (iii) printing, preferably screen-printing, the printable ink onto the substrate, and
- (iv) at least partly removing the solvent.

This screen-printed electrode on the conductive carbon substrate is a technology aimed at unconventional supercapacitor device manufacture, which is inexpensive, rapid, and capable of mass production.

Yet another embodiment of the present invention provides a supercapacitor comprising an electrode as described herein.

25 The industrial NGP/PANI two-electrode supercapacitor exhibited high performance up to 305 F/g, when comparing with other supercapacitors using graphene/PAni composite electrode. Furthermore, the supercapacitor as described herein shows a good cycling stability.

Detailed description of the Invention

30 The printable NGP/PAni ink composition comprises nano graphene platelets (also referred to as "NGP"), a polymer comprising aniline monomeric units, at least one solvent, optionally a binder and optionally further additives.

35 The viscosity of the printable ink generally depends on the printing method. For the preferred screen printing method, viscosities of from 10 mPa s to 50 000 mPa s are preferred. Particularly preferred are viscosities of from 500 mPa s to 50000 mPa s. The shear rate dependency of the ink viscosity is shown in Fig. 4. It can be seen that the inks exhibit a shear-thinning effect.

40 Preferably the printable ink consists of nano graphene platelets, polyaniline, a solvent and optionally a binder.

Graphene is a monolayer of carbon atoms arranged in a two-dimensional honeycomb network. "Nano graphene platelets" in the terms of the present invention is however not restricted to a material consisting exclusively of single-layer graphene (i.e. graphene in the proper sense and according to the IUPAC definition), but, like in many publications and as used by most commercial providers, rather denotes a bulk material, which is generally a mixture of a single-layer material, a bi-layer material and a material containing 3 to 10 layers and sometimes even more than 20 layers ("few layer graphene"). The ratio of the different materials (single, bi and multiple layers) depends on the production process and provider. In case of the present invention, the material termed "nano graphene platelets" is characterized by the absence of the graphite peak in the XRD: The degree of exfoliation of the graphene material being related to the layer thickness can be monitored by XRD (X-ray diffraction). The presence of the reflection at $2\theta = 25$ to 30° (with Cu $K\alpha$ radiation, X-ray wavelength = 0.154 nm; the precise value is 26.3° , but often only a broad band instead of a sharp peak is obtained) originates from the layered structure and thus relates to the amount of native graphite. Preferably, the graphene of the invention does not reveal a graphite peak related to the stacking and thus unexfoliated material.

"nano graphene platelets" in terms of the present invention are further characterized by a low bulk density of preferably at most 0.2 g/cm^3 , e.g. from 0.001 to 0.2 g/cm^3 or from 0.003 to 0.2 g/cm^3 , more preferably at most 0.15 g/cm^3 , e.g. from 0.001 to 0.15 g/cm^3 or from 0.003 to 0.15 g/cm^3 , even more preferably at most 0.1 g/cm^3 , e.g. from 0.001 to 0.1 g/cm^3 or from 0.003 to 0.1 g/cm^3 , in particular at most 0.05 g/cm^3 , e.g. from 0.001 to 0.05 g/cm^3 or from 0.003 to 0.05 g/cm^3 , and specifically at most 0.01 g/cm^3 , e.g. from 0.001 to 0.01 g/cm^3 or from 0.003 to 0.01 g/cm^3 .

"Nano graphene platelets" in terms of the present invention are moreover characterized by a high BET (Brunauer-Emmett-Teller) surface area. Preferably, the BET area is at least $200 \text{ m}^2/\text{g}$, e.g. from 200 to 2600 or from 200 to 2000 or from 200 to $1500 \text{ m}^2/\text{g}$ or from 200 to $700 \text{ m}^2/\text{g}$; more preferably at least $300 \text{ m}^2/\text{g}$, e.g. from 300 to 2600 or from 300 to 2000 or from 300 to 1500 or from 300 to $700 \text{ m}^2/\text{g}$.

"Nano graphene platelets" are preferably characterized by a high ratio of carbon to oxygen atoms (C/O ratio): The elemental composition as expressed by the ratio of carbon to oxygen atoms (C/O ratio) is related to the degree of chemical reduction of the graphene material. The C/O ratio is preferably at least 3:1, more preferably at least 5:1, even more preferably at least 50:1, particularly preferably at least 100:1 and in particular at least 500:1, as determined e. g. from the atomic percentages (at%) of the elements via X-ray photoelectron spectroscopy (XPS).

Nano graphene platelets employed within the inks according to the present invention as such are known to a person skilled in the art. Several methods for producing such NGPs are known, such as but not limited to the exfoliation and wet-chemical reduction of graphite oxide prepared by a modified Hummer's or Staudenmeier's method (ACS Nano 2008, 2 (3), 463-470; Nano

Letters 2010, 10 (12), 4863-4868), the thermal shock exposure exfoliation method for graphite oxide (J. Phys. Chem. B, 2006, 110 (17), 8535-8539 and McAllister, M. J. et al.; Chem. Mater. 2007, 19, 4396-4404, Macromolecules 2010, 43, pages 6515 to 6530 and WO 2009/126592) the epitaxial growth on silicon carbide (Nature Materials 2009, 8 (3), 203-207), or chemical
5 vapor deposition (Nano Letters 2009, 9 (1), 30-35).

Preferably, the NGP are prepared by reduction of graphene graphite oxide by athermal shock exposure exfoliation method as described in US 2010/0056819 A1 and US 2010/055025 A1 that leads to a simultaneous exfoliation and reduction of the graphite oxide feedstock. In
10 contrast to other methods involving hazardous reducing agents (such as e. g. hydrazine monohydrate) and which is not suitable for industry scale reduction, the thermal reduction of graphite oxide is much more environment-friendly and offers the possibility for large scale production. This is for example illustrated in Nature Nanotechnology 4, 612 - 614 (2009). Typically, the NGPs obtainable by the thermal shock exposure exfoliation method reveal a
15 crumpled, sheet-like morphology as shown in Figs. 5 and 6 that is in contrast to NGPs obtained from the wet-chemical exfoliation and reduction of graphite oxide and which are typically of a fully planar nature. As it can be seen in Figs. 5 and 6, the electron microscopy analysis reveals that the overall atomically thin and translucent sheets display large wrinkles and folds that are distributed over the surface of the individual NGPs. In the literature the formation of these
20 characteristic wrinkles has been ascribed to the fast thermal reduction of adjacent epoxy sites that are present within the graphite oxide raw material leaving no time for the NGPs to readopt a fully planar conformation (J. Phys. Chem. B, 2006, 110 (17), 8535-8539). A useful side-effect of the wrinkled nature of the NGPs prepared by the thermal shock exposure exfoliation method is that it prevents the re-stacking and reaggregation of the NGPs. NGPs prepared by the
25 thermal shock exposure exfoliation method can also be easily identified from morphological analysis studies.

Based on the different energy storage mechanisms, supercapacitors can be divided into two
30 classes: 1) electrochemical double-layer capacitors (EDLCs) which store energy using the adsorption of both anions and cations, And 2) pseudo-capacitors that store energy through fast surface redox reactions.

The capacitance in graphene based EDLC devices is stored as a build-up of ion charge in the layers of the electrical double-layer formed at the interface between a high-surface area
35 electrode and an electrolyte. The larger graphene surface area, the larger ion can be adsorbed on the graphene surface.

The platelets generally have dimensions in the nanometer scale, preferably of from about 50 nm × 50 nm to about 10000 nm × 10000 nm.

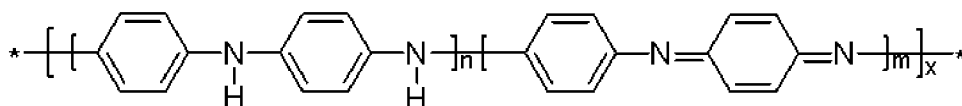
The electrical conductivity of the graphene composites should generally be of from about 1×10^2 S/cm to about 5×10^{-1} S/cm (powder conductivity measured at 500 bar on compressed pellets).

- 5 The concentration of the nano graphene platelets in the printable ink may generally be of from about 0.05% by weight to about 10 % by weight, preferably of from about 0.1 % by weight to about 5% by weight, most preferably of from about 0.5 % by weight to about 2.5% by weight.

10 The printable ink comprises a polymer comprising an aniline monomer unit. Such polymers may be homopolymers of aniline or copolymers of aniline with other monomeric units, in the following both also referred to as "Polyanilines". Preferably the polymer consists of aniline homopolymers.

Polyanilines are polymerized from the inexpensive aniline monomer. Aniline homopolymers can be described by the formula I:

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20 Preferably the polyaniline is in its emeraldine ($n = m = 0.5$) form. The emeraldine base (EB) is neutral and, if doped (protonated) it is called emeraldine salt (ES), with the amine nitrogens protonated by an acid. Protonation is necessary to delocalize the otherwise trapped diiminoquinone-diaminobenzene state. The production of aniline homopolymers is well known in the art and available from several sources in the market. Preferably the emeraldine salt aniline homopolymer is used.

- 25 Generally the molecular weight M_w of polyaniline may be of from about 1000 g/mol to about 200000 g/mol, preferably of from about 2000 g/mol to about 100000 g/mol, most preferably of from about 5000 g/mol to about 50000 g/mol.

30 Besides the homopolymers copolymers of aniline may be used. Such copolymers may be but are not limited to copolymers of aniline and N-phenylglycine, copolymers of aniline and alkylaniline, copolymers of aniline and N-4(sulfophenyl)aniline and any other electrically conducting copolymer.

35 The concentration of the polyaniline in the printable ink may generally of from about 0.1 % by weight to about 20 % by weight, preferably of from about 0.2 % by weight to about 10 % by weight, most preferably of from about 0.5 % by weight to about 5.0 % by weight.

The weight ratio between the NGPs and the polyaniline may generally be from 1:10 to 10:1, preferably from 1:5 to 5:1, more preferably from 1:3 to 1:1, most preferably 1:2 to 1:1.5.

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The printable ink further comprises at least one solvent.

The solvent should be capable of solving the polyaniline and optionally the binder. Furthermore the solvent should be capable of forming a stable dispersion of graphene in the presence of the polyaniline. Last not least the solvents need to be vaporizable in order to be removed from the deposited ink to form the electrode layer. Preferably, the boiling point (at atmospheric pressure) of the solvent is below about 200 °C, preferably from about 50 °C to about 150 °C, most preferably from about 70 °C to about 120 °C.

The solvent may be a protic or aprotic polar organic solvents or water.

10 Protic polar solvents may be selected from C₁ to C₆ alkanols, preferably methanol, ethanol or propanol. In a particular embodiment the protic organic solvents have a low water content and are most preferably essentially water-free. A low water content as used herein means that the water content of the solvent is below 5 %, preferably below 3 %.

15 Aprotic polar solvents may be selected from

- (a) Nitrogen containing solvents, such as but not limited to N-methyl-2-pyrrolidone, N-ethyl-2-pyrrolidone dimethylformamide, and dimethylacetamide (DMAC),
- (b) Aromatic solvents, such as but not limited to 3-methylphenol (m-cresol),
- (c) sulfoxides, such as but not limited to dimethyl sulfoxide (DMSO).

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Most preferably the solvent is selected from ethanol, N-methyl-2-pyrrolidone, dimethylformamide, and water.

Also combinations of the said solvents may be used as long as they form a one phase solution.

25 Preferable only one solvent is used.

The amount of the solvent in the printable ink may generally be of from about 1 % by weight to about 99 % by weight, preferably of from about 50 % by weight to about 99 % by weight, most preferably of from about 95 % by weight to about 99 % by weight.

30 The printable ink may preferably comprise a binder in order to adjust the viscosity of the ink and to improve the adhesion interaction between the ink and the substrate.

Suitable binders are selected from organic polymers, including water-soluble and water-insoluble organic polymers, whereby the expression polymers does also encompass

35 copolymers. Preferred water-insoluble polymers are fluorinated polymers such as polyvinylidene fluoride, polyvinyl fluoride, polytetrafluoroethylene, copolymers from tetrafluoroethylene and hexafluoro propylene, copolymers from vinylidene fluoride and hexafluoro propylene or copolymers from vinylidene fluoride and tetrafluoroethylene. For the purpose of the present invention, vinylidene fluoride can also be referred to as vinylidene difluoride, and polyvinylidene fluoride can also be referred to as polyvinylidene difluoride. A particularly preferred water-soluble binder is polytetrafluoroethylene (PTFE).

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5 The concentration of the binder in the printable ink may generally be of from about 0 % by weight to about 10 % by weight. In one embodiment the concentration of the binder is about 0 % by weight. In another embodiment the concentration of the binder is from about 0.01 % by weight to about 5 % by weight, most preferably of from about 0.1 % by weight to about 2.5 % by weight.

10 Further additives may be present in the printable ink. Such additives may be, but are not limited to surfactants and conducting additives, such as but not limited to carbon black. Preferably the ink is free from carbon black, most preferably free from any carbon material except the NGP.

Useful surfactants may be anionic, cationic nonionic or amphoteric surfatants. Particularly preferred are anionic surfactants, such as but not limited to sodium dodecylbenzenesulfonate (SDBS).

15 Another embodiment of the present invention is a composite material comprising nano graphene platelets, polyaniline, optionally a binder, and optionally a surfactant as described herein.

20 The capacitance is an important parameter of an electrode and a supercapacitor comprising such composite material. Generally, the higher the capacitance the better is the performance. The composite material preferably has a capacitance of 100 F g⁻¹ or more, more preferably of 200 F g⁻¹ or more, most preferably of from 300 F g⁻¹ or more. The capacitance can be determined, e. g. according to J. R. Miller and A. F. Burke, Electric Vehicle Capacitor Test, Procedures Manual, Idaho National Engineering Laboratory, Report No. DOE/ID-10491, 1994, and/or according to R. B. Wright and C. Motloch, Freedom CAR Ultracapacitor Test, Manual, Idaho National Engineering Laboratory, Report No. DOE/NE ID-11173, 2004.

30 Another subject of the present invention is an electrode comprising at least one composite material as described above and at least one binder.

The concentration of the NGPs in the electrode may generally be of from about 10 % by weight to about 95 % by weight, preferably of from about 20 % by weight to about 80% by weight, most preferably of from about 30 % by weight to about 60% by weight.

35 The concentration of the polyaniline in the electrode may generally of from about 10 % by weight to about 95 % by weight, preferably of from about 20 % by weight to about 80 % by weight, most preferably of from about 60 % by weight to about 30 % by weight.

40 The concentration of the binder in the electrode may generally be of from about 0 % by weight to about 30 % by weight, preferably of from about 0 % by weight to about 20 % by weight, most preferably of from about 5 % by weight to about 10 % by weight.

In one particular embodiment of the present invention, the electrode comprises

- (a) in the range of from 50 to 95 % by weight of the composite material, preferably 75 to 90 % by weight,
- (b) in the range of from 1 to 20 % by weight binder, preferably 5.0 to 10 % by weight,
- 5 (c) a total in the range of from zero to 20 % by weight additive(s), preferably 7.5 to 15 % by weight,

referring to the total sum of components of said inventive electrode.

10 Usually the printed electrode has a thickness of from about 1 μm to about 100 μm , preferably from about 3 μm to about 50 μm , most preferably from 5 to 15 μm .

The electrodes may be connected through one or more current collectors to at least one other component of the capacitor. In the context of the present invention, said current collector will not be considered as component of the electrode according to the present invention.

15

The electrodes may further comprise a backbone, such as a metal foil or a metal gauze. Suitable metal foils can be made from, e. g., nickel. Suitable metal gauze can be made from steel, in particular from stainless steel. In the context of the present invention, said current backbone will not be considered as component of the electrode according to the present invention.

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The electrode according to the present invention may further comprise an electrolyte which is preferably a PVA/H₂SO₄ gel (a gel made of polyvinyl alcohol and H₂SO₄), a PVA/H₃PO₄ gel, a PVA/KOH gel, a PVA/NaOH gel, a PVA/Na₂SO₄ gel, a ionic liquid polymer gel or any other organic polymer based electrolyte. The before-mentioned gels are known to a person skilled in the art. Ionic liquid polymer gels as such and methods for producing said ionic liquid polymer gels are described, for example, in S.M. Zakeeruddin and M. Grätzel, Adv. Fund. Mater. (2009), 19, pages 2187-2202, in particular under section 6.

25

30 In case an ionic liquid polymer gel is employed within the present invention, it is preferred to employ at least one ionic liquid of the formula 1-alkyl-3-methylimidazolium halide, wherein alkyl is preferably C₃ to C₉-alkyl and/or halide is preferably iodide. As polymer or gelator within said ionic liquid polymer gel it is preferred to employ a low molecular weight polymer (gelator) such as poly(vinylidene fluoride-co-hexafluoropropylene).

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More preferably, the electrolyte is a PVA/H₂SO₄ gel. It is also preferred that the electrode according to the present invention is obtained by cutting the aerogel into slices having a thickness of 0.5 to 1.5 mm and/or having a diameter of 5 to 15 mm.

40 According to a further embodiment of the present invention the electrode is free of any electrolyte.

A further embodiment of the present invention is a process for preparing a conducting ink, comprising

- (a) providing a dispersion of at least partly exfoliated nano graphene platelets in a solvent,
- (b) providing a polymer comprising aniline monomeric units soluble in the solvent,
- 5 (c) optionally providing a binder, and
- (d) combining the products of steps (a), (b) and optionally (c) in any order to form the printable ink.

10 The process may very simply be performed in one vessel. It is not necessary to have any reworking steps but the ink may be used "as is". The simplicity of the process is a major advantage over the ink preparing processes as described in the prior art. In the state of the art approaches multiple graphite oxide washing, purification, centrifugation, filtration, reduction and drying steps are part of the preparative procedure.

15 Step (a) may be performed by any method in which shearing forces are applied to the NGPs in order to exfoliate and disperse the NGPs in the solvent. By way of example, ball milling of NGPs in the solvent may be used for a time sufficient to at least partly, preferably essentially, most preferably completely exfoliate the nano graphene platelets (i.e. to produce singly layered graphene sheets).

20 The polyaniline in step (b) may be provided in pure form or as a solution in a solvent. Preferably the polyaniline is provided as a solution in the solvent as used in step (a).

25 The binder in step (c) may be provided in pure form or as a solution in a solvent. Preferably the binder is provided as a solution in the solvent as used in step (a).

It is preferred to apply shearing forces during at least one of steps (a), (b), (c) and (d).

30 Yet another embodiment of the present invention is a process for preparing an electrode, comprising

- (i) providing a printable ink as describe above,
- (ii) providing a substrate,
- (iii) depositing the printable ink onto the substrate,
- 35 (iv) at least partly removing the solvent.

The quality of screen-printed thin films depends highly on printing conditions including printing speed, ink stability and especially ink viscosity. The printable inks used herein all exhibit good shear-thinning behavior.

40 The substrate according to step (ii) may be selected from a metal foil, conductive cloth; conductive carbon fabrics and a flexible conductive fabric. By way of example, carbon fabrics may be made from cotton yarns coated with a solution based on carbon black. A conductive

fabric or cloth consist of a non-conductive or less conductive substrate, which is either coated or embedded with electrically conductive elements, often carbon, nickel, copper, gold, silver, or titanium. Substrates typically include cotton, polyester, nylon, and stainless steel as well as high performance fibers such as aramids.

- 5 By way of example, conductive carbon substrates may be derived from polyacrylonitrile (PAN) precursor. It combines electrically conductivity, high strength, low modulus of elasticity and low density for maximum performance. Preferably the conductive carbon substrate is flexible. "Flexible" as used herein means that the modulus of elasticity of the substrate is below 5 kN/mm², preferably below 2 kN/mm².

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Preferably the substrate is selected from a conductive carbon fabric and a flexible carbon substrate, most preferably the substrate is a flexible carbon substrate.

- 15 The deposition in step (iii) may be performed by any common liquid deposition method, preferably by printing, most preferably by screen-printing.

During deposition by screen printing, the screen is generally placed a few millimeters above the surface of the substrate. After loading the NGP/PAni ink onto the screen, a rubber "squeegee" is swept across the surface of the screen thus bringing it into close contact with the substrate. At this point, the ink flows from the screen to the surface of the substrate. As the squeegee then
20 passes over a region, the screen separates from the substrate, leaving behind ink that dries to yield a continuous film.

- To form the NGP/PAni layer on the substrate, the solvent has to be at least partly removed in step (iv). This can simply be done by evaporation at room temperature or supported by
25 increased temperature or reduced pressure. Finally, the residual solvent should not exceed 3 % by weight, preferably, 1 % by weight, most preferably 0.1 % by weight.

The composite material prepared by using the inks according to the invention may advantageously be used in capacitors, particularly supercapacitors.

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Therefore a further embodiment of the present invention is a supercapacitor, also called electric double-layer capacitor comprising a composite material prepared by using the printable ink or an electrode as described above.

- 35 Supercapacitors as such are well known in the art. They are useful for the energy storage and power delivery solutions for automotive, heavy transportation, uninterruptible power system.

If a conductive substrate is used as the current collector directly, it is easier and more efficient compared to the conventional supercapacitor electrode fabrication where the active electrode
40 material is pressed on a Ni foam current electrode. As the carbon substrate may be used as the current collector, the NGP/PAni based thin film supercapacitor is more flexible and light-weight

comparing with conventional supercapacitor device in which Pt or Ni is used as current collectors.

5 The composite material and the electrodes as described herein may also advantageously be used in gas sensor applications.

All percent, ppm or comparable values refer to the weight with respect to the total weight of the respective composition except where otherwise indicated. All cited documents are incorporated herein by reference.

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Brief description of the Figures

Fig. 1a shows the double electrode capacitor setup according to example 2.

Fig. 1b shows the flexible double electrode capacitor setup according to example 3.

15 Fig. 2 shows the capacitance of the respective electrodes according to example 2.

Fig. 3 shows the cycling stability of NGP and NGP/PAni supercapacitor device over 1000 cycles, cycling stability measured at a constant current 5 mA, with 1M H₂SO₄ electrolyte according to example 2. Inset: Galvanostatic charge-discharge curves of NGP/PAni_{1:1.5} electrodes.

20 Fig. 4 shows the dependency of the ink viscosity as a function of shear rate for NGP, PAni and various weight ratios between the NGP and PAni.

Fig. 5 shows a SEM study of the carbon fabric substrate (A, B); NGP (C,D) and NGP/PAni 1:1.5 . (E,F). The white arrows in F indicate the PAni particles on the NGP surface.

Fig. 6 shows a TEM picture of an individual NGP flake.

25

The following examples shall further illustrate the present invention without restricting the scope of this invention.

Examples

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Materials:

Graphene N002-PDR (average thickness 1-10 nm) was purchased from Angstrom Materials Inc. (Dayton, OH, United States of America), Polyaniline (emeraldine base, average M_w ~5,000 g/mol) was purchased from Sigma-Aldrich. PTFE (60% in water) was purchased from DuPont. 35 The carbon fabric (34BA) was purchased from SGL Carbon. The flexible carbon substrate (H2315 IX 11) was purchased from Freudenberg & Co.

Instruments and measurements:

40

Ball milling experiments were carried out using a Dispermat ball miller from Vma-Getzmann GmbH. The milling ball material was ZrO₂ 68% (SAZ-Zirkonmischoxid ER 120 S). The printing experiments were carried out using a fully automated Screen Printer (Alraun Technik, AT 701

M) with Sefar screen mesh (32-100W PW). The viscosity was measured by HAAKE analytical instruments, using a 60 mm Ø, 0.50 cone and plate. Scanning electron microscope (SEM) measurements were carried out with a Zeiss Ultra 55 (FE-SEM), operated at 5 kV. Nitrogen adsorption and desorption isotherm measurements were carried out at 77 K with a
5 Quantachrom Autosorb 6B analyzer.

All electrochemical measurements were carried out using 1 M H₂SO₄ as the electrolyte.

Example 1

10 A series of homogenous NGP and NGP/PAni inks were prepared by ball milling method. The weight ratio of NGP, PAni and PTFE was varied as 90:0:10, 60:30:10, 45:45:10, 36:54:10, 30:60:10. The resulting inks are labelled as NGP, NGP/PAni_{1:0.5}, NGP/PAni_{1:1}, NGP/PAni_{1:1.5}, NGP/PAni_{1:2}, respectively. Typically, for the ink labelled as NGP/PAni_{1:1.5}, ethanol (200 ml),
15 milling ball (130 ml) and NGP powder (2.13 g) were added to a stainless steel capsule. The mixture was then placed under the shearing forces at a speed of 5500 rpm for 1 hour, at 10 °C . After this process, PAni (3.23 g) was added to the above mixture, and ball milling was carried out for 10 minutes. Finally, PTFE (1 g, 60% by weight in water) was added, again, ball milling was carried out for another 10 minutes, and the NGP/PAni_{1:1.5} ink was then obtained. Other inks
20 were made by varying the weight accordingly.

The NGP/PANI inks used herein all exhibited good shear thinning behavior with a viscosity of around 125 mPa s observed at a shear rate of 10 s⁻¹. These viscosity results fit to the screen-printing requirements.

25

Example 2

Two-electrode supercapacitors were fabricated as these devices best represent those commonly produced commercially.

30

In a symmetric two-electrode system, the NGP/PAni electrodes (diameter 2 cm) on a hard carbon fabric substrate were assembled in a stainless steel supercapacitor cell with titanium current collectors. The two-electrode supercapacitor was built using a sandwich type construction (electrode/glass microfiber filter separator/electrode, see Fig. 1a).

35

The ink was printed on the carbon fabric substrate as follows: During screen printing deposition, the screen mask was placed a few millimeters above the surface of the carbon fabric substrate. After loading the NGP/PAni ink onto the screen, a rubber “squeegee” was swept with a velocity of 35 cm/s across the surface of the screen thus bringing it into close contact with the substrate.
40 At this point, the ink flew from the screen to the surface of the substrate. As the squeegee then passed over a region, the screen separated from the substrate, leaving behind ink that dried to yield a continuous film. A thin film with dimensions of 4 cm × 3 cm could be fabricated in a very

short timescale of just 0.1 seconds. The ability to produce thin films of high quality on this short timescale is highly desirable in industrial applications.

The current density as a function of the potential of the respective electrodes is shown in Fig. 2.

- 5 At a scan rate of 20 mV s^{-1} , NGP, NGP/PAni_{1:0.5}, NGP/PAni_{1:1}, NGP/PAni_{1:1.5} and NGP/PAni_{1:2} deliver specific capacitances of 26, 85, 190, 269, and 177 F g^{-1} , respectively, based on the active materials mass of two electrodes (including the mass of PTFE binder).

- 10 Nitrogen adsorption-desorption analysis revealed a typical Brunauer–Emmett–Teller specific surface area of the NGP, NGP/PAni_{1:0.5}, NGP/PAni_{1:1}, NGP/PAni_{1:1.5}, NGP/PAni_{1:2}, are 497, 260, 232, 215, 184 $\text{m}^2 \text{g}^{-1}$, respectively, while the specific surface area for the pure PAni is 34 $\text{m}^2 \text{g}^{-1}$.

The NGP/PAni_{1:1.5} supercapacitors showed the best specific capacitance of 269 F g^{-1} , power density of 454 kW kg^{-1} and energy density of 9.3 Wh kg^{-1} , operating in 1M H_2SO_4 electrolytes.

- 15 The supercapacitor showed excellent cyclic stability with no degradation over 1000 charge/discharge cycles as shown in Fig. 3.

Example 3

- 20 For a flexible supercapacitor, two of the NGP/PAni PAni_{1:1.5} thin film electrodes ($2.3 \text{ cm} \times 2.6 \text{ cm}$) on a flexible carbon substrates were used as the active electrodes, and the flexible carbon substrate was used as the current collector. A separator (glass microfiber filter paper) was placed between the two electrodes (electrode/glass microfiber filter separator/electrode). The device was thermally encapsulated within a laminated pouch. The device structure using a sandwich type construction (electrode/separator/electrode) is shown in Fig. 1b.

- 30 The ink was printed on the flexible carbon substrate as follows: During screen printing deposition, the screen mask was placed a few millimeters above the surface of the flexible carbon substrate. After loading the NGP/PAni ink onto the screen, a rubber “squeegee” was swept with a velocity of 35 cm/s across the surface of the screen thus bringing it into close contact with the substrate. At this point, the ink flew from the screen to the surface of the substrate. As the squeegee then passed over a region, the screen separated from the substrate, leaving behind ink that dried to yield a continuous film. A thin film with dimensions of $4 \text{ cm} \times 3 \text{ cm}$ could be fabricated in a very short timescale of just 0.1 seconds. The ability to produce thin films of high quality on this short timescale is highly desirable in industrial applications.

The performance of the NGP/PAni_{1:1.5} flexible supercapacitors are well-retained over the bending 200 cycles.

Claims

1. A screen-printable ink comprising
 - (a) nano graphene platelets,
 - (b) a polymer comprising aniline monomeric units,
 - (c) at least one solvent.
2. The screen-printable ink according to claim 1, wherein the polymer consists of polyaniline.
3. The screen-printable ink according to claim 1 or 2, the graphene platelets are prepared by reduction of graphene oxide.
4. The screen-printable ink according to anyone of the preceding claims, the graphene platelets having a surface area of 300 m²/g or more.
5. The screen-printable ink according to anyone of the preceding claims, wherein the solvent is a protic or aprotic polar solvent.
6. The screen-printable ink according to claim 6, wherein the solvent is selected from C₁ to C₆ alkanols, water, nitrogen containing solvents, aromatic solvents, and sulfoxides.
7. The screen-printable ink according to anyone of the preceding claims, further comprising a binder.
8. The screen-printable ink according to anyone of the preceding claims, having a viscosity of from 500 mPa s to 50000 mPa s.
9. A process for preparing a screen-printable ink according to anyone of the preceding claims comprising
 - (a) providing a dispersion of at least partly exfoliated nano graphene platelets in a solvent,
 - (b) providing a polymer comprising aniline monomeric units, said polymer being soluble in the solvent,
 - (c) optionally providing a binder, and
 - (d) combining the products of steps (a), (b) and optionally (c) in any order to form the screen-printable ink.
10. The process according to claim 9, wherein nano graphene platelet dispersion, the polyaniline, and optionally the binder are combined in step (d) in one vessel.
11. A composite material deposited on a substrate by using a screen-printable ink according

to anyone of claims 1 to 8.

12. Use of a composite material according to claim 11 in capacitors.
- 5 13. An electrode comprising a composite material according to claim 11 deposited on a substrate.
14. The electrode according to claim 13, wherein the substrate is selected from metal foil, conductive cloth, conductive carbon fabrics, and a flexible conductive fabric.
- 10 15. A process for preparing an electrode, comprising
- (i) preparing a screen-printable ink according to anyone of claims 9 or 10,
 - (ii) providing a substrate,
 - (iii) depositing the screen-printable ink onto the substrate,
 - 15 (iv) at least partly removing the solvent.
16. A capacitor comprising an electrode according to claim 13 or 14.

Fig. 1a

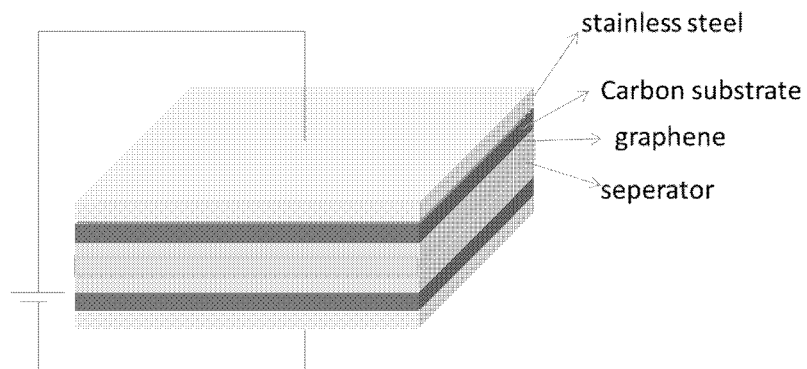


Fig. 1b

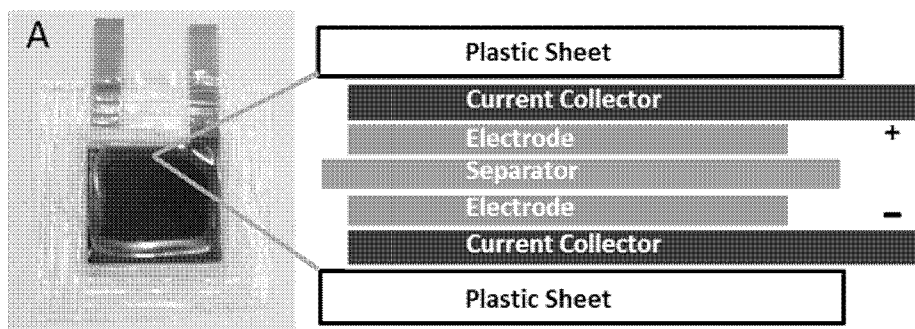


Fig. 2

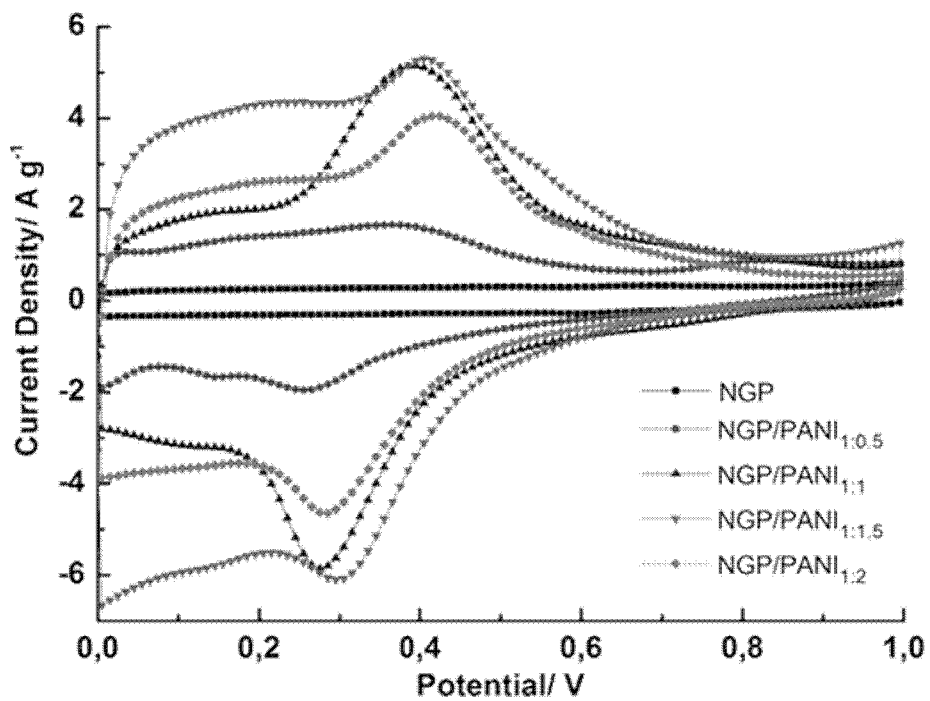


Fig. 3

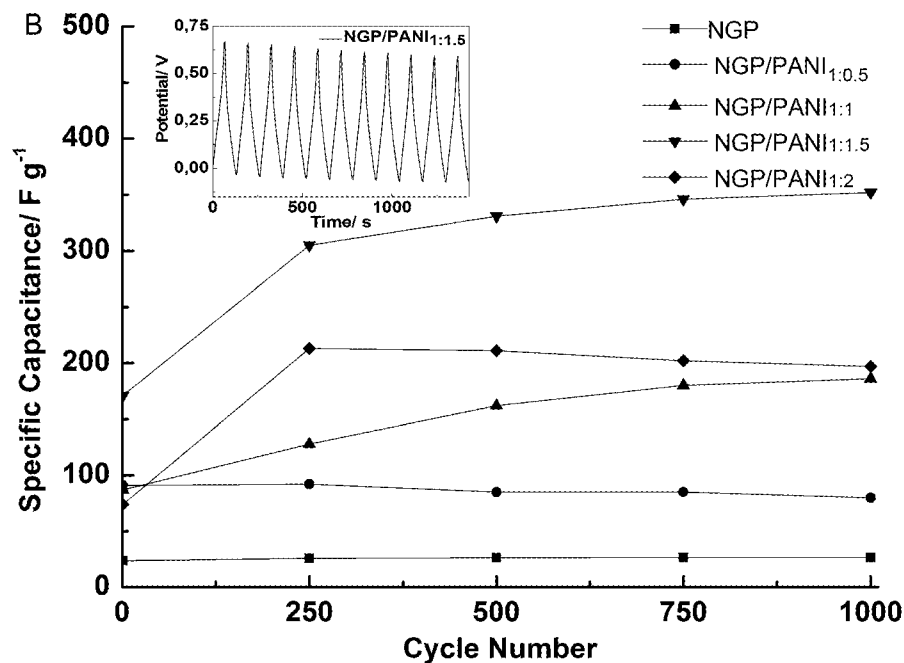


Fig. 4

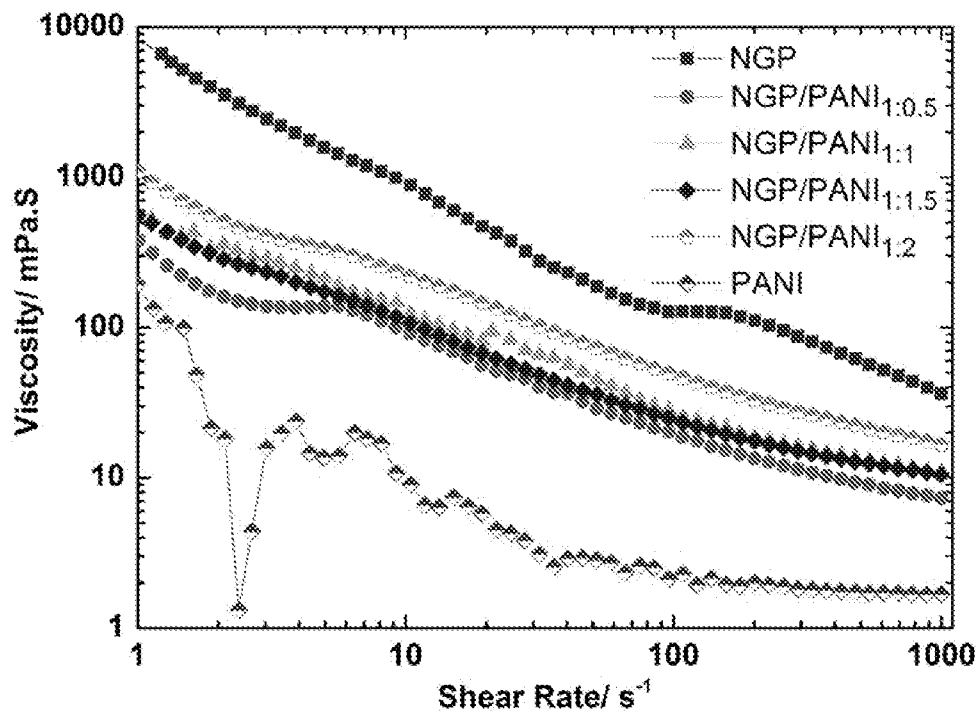


Fig. 5

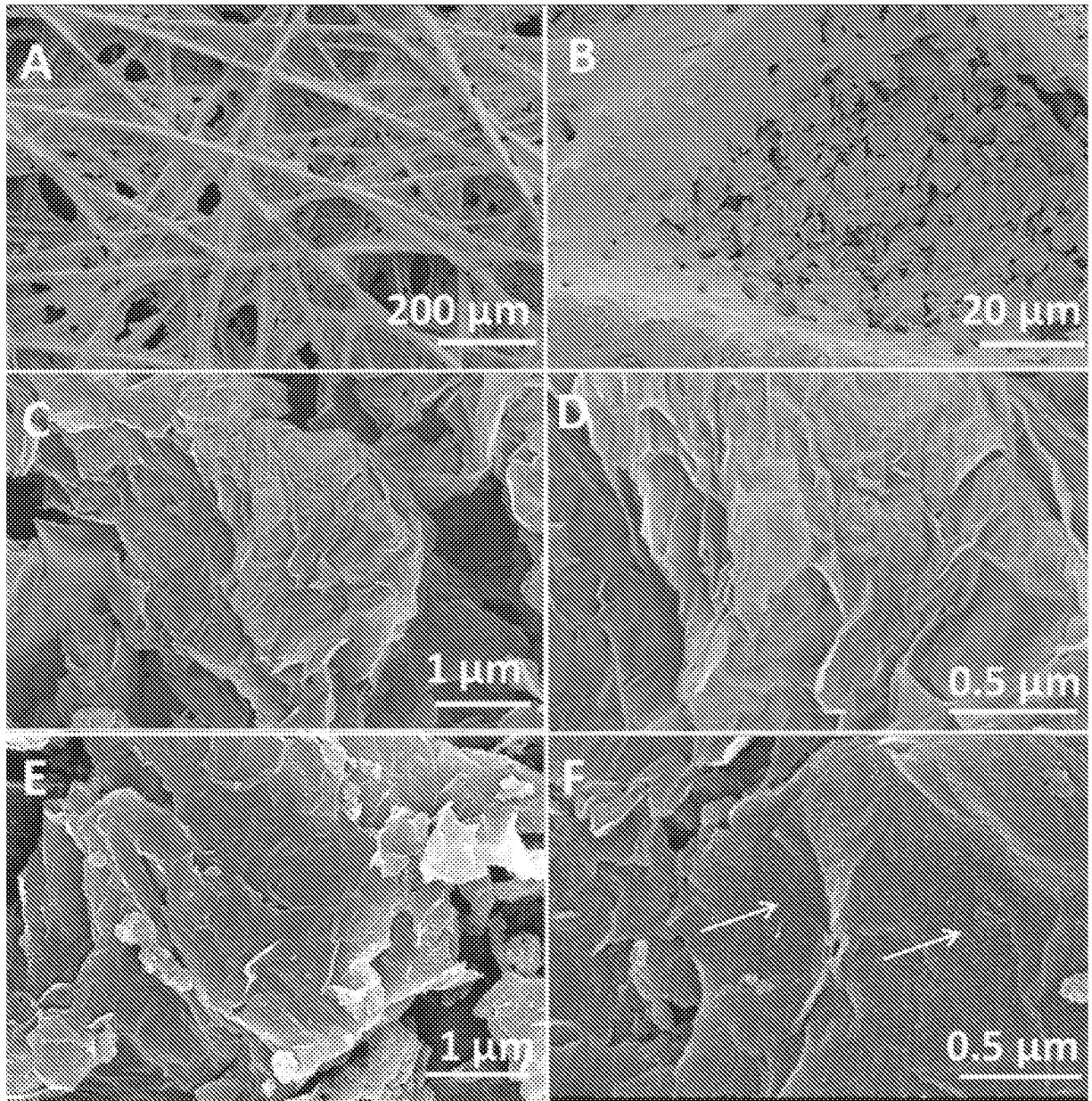


Fig. 6

