

MULTILAYER FILM COMPRISING METAL NANOPARTICLES AND A GRAPHENE-BASED MATERIAL AND METHOD OF PREPARATION THEREOF

CROSS-REFERENCE TO RELATED APPLICATIONS

5 [001] This application makes reference to and claims the benefit of priority of an application for "Method of Preparing Multi-layered Hybrid Nano-architectures Based on Reduced Graphene Oxide" filed on April 7, 2011, with the United States Patent and Trademark Office, and there duly assigned serial number 61/472,838. The content of said application filed on April 7, 2011, is incorporated herein by reference in its entirety for all
10 purposes.

TECHNICAL FIELD

[002] The invention relates to a multilayer film comprising metal nanoparticles and a graphene-based material, and a method of preparing the multilayer film.
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BACKGROUND

[003] Graphene and metal nanoparticles have been used as nano-building blocks for assembly into macroscale hybrid structures with some promising performance in nanoelectronics. A critical challenge in building these graphene-based macroscale structures
20 relates to realization of the transfer of the exceptional properties of the graphene nanosheets to the macroscale structures, as state of the art methods to fabricate these structures lack good control with regards to the reaction process, as well as orientation of the building blocks, and organization of the structures at the nanoscale.

[004] Among various macroscale structures, free-standing paper-like structures, such as
25 multilayer films, have attracted extensive interest because of their unique catalytic, electrochemical and mechanical properties, which render them suitable for applications in chemical filters and electrode materials for energy storage. Of particular interest is application of the graphene-based structures in flexible supercapacitor devices with large power and energy densities, as these flexible supercapacitor devices have many potential
30 applications in portable electronic devices. However, the strong π - π stacking and van der Waals forces between the planar basal planes of graphene sheets often result in self-agglomeration of the graphene sheets during fabrication of the graphene-based multilayer

structures. As a result, the aggregated structures behave like particulate graphite platelets and lose the ultra-high surface area characteristic unique to graphene sheets. This deleteriously affects the potential applications of graphene-based multilayer films in the fields of supercapacitors and batteries.

5 [005] Various groups have attempted to incorporate transition metal oxides and conducting polymer to paper-like graphene-based hybrid films to separate the graphene sheets and improve the supercapacitor electrode performance. However, poor conductivity of the transition metal oxides and conducting polymers increased the resistance of graphene-based hybrid film electrodes, limiting them from usage in flexible supercapacitors with high
10 power density.

[006] In view of the above, there is a need for an improved method to prepare a graphene-based multilayer film that overcomes at least some of the above drawbacks.

SUMMARY OF THE INVENTION

15 [007] In a first aspect, the invention relates to a method of the preparation of a multilayer film comprising metal nanoparticles and a graphene-based material using electrophoretic deposition. The method comprises

- a) electrophoretically depositing a layer of graphene-based material on a substrate;
- b) electrophoretically depositing a layer of metal nanoparticles on the layer of
20 graphene-based material;
- c) optionally repeating steps (a) and (b) for one or more additional cycles; and
- d) depositing a layer of graphene-based material on the layer of metal nanoparticles.

[008] In a second aspect, the invention relates to a multilayer film comprising metal nanoparticles and a graphene-based material obtainable by the method according to the first
25 aspect.

[009] In a third aspect, the invention relates to a multilayer film comprising a layer of metal nanoparticles between a first layer of a graphene-based material and a second layer of a graphene-based material

[0010] In a fourth aspect, the invention relates to an electrode comprising a multilayer
30 film according to the second aspect or the third aspect.

BRIEF DESCRIPTION OF THE DRAWINGS

[0011] The invention will be better understood with reference to the detailed description when considered in conjunction with the non-limiting examples and the accompanying drawings, in which:

5 [0012] **Figure 1** is a series of schematic diagrams showing (A) a general scheme depicting electrophoretic deposition of (I) a graphene-based material, and (II) metal nanoparticles; and (B) electrophoretic deposition of (I) graphene oxide (GO), and (II) gold nanoparticles (AuNP) according to various embodiments of the invention.

10 [0013] **Figure 2** is a series of schematic diagrams depicting the formation of multilayer graphene oxide/gold nanoparticle (GO/AuNP) film, and subsequent chemical reduction of the multilayer GO/AuNP film to reduced graphene oxide/gold nanoparticle (RGO/AuNP) film according to embodiments of the invention. (A) A layer of graphene oxide is coated on an ITO coated glass substrate; (B) a layer of gold nanoparticles is coated on the layer of graphene oxide; (C) a layer of graphene oxide is coated on the layer of gold nanoparticles;

15 (D) the multilayer GO/AuNP film is chemically reduced to a multilayer RGO/AuNP film using a reducing agent such as hydrazine monohydrate.

[0014] **Figure 3** is an optical image of (A) GO in dimethylformamide (GO-DMF) suspension, and (B) gold nanoparticles in dimethylformamide (AuNP-DMF) suspension.

20 [0015] **Figure 4** is Raman spectrum of multilayer hybrid film after and before reduction, for (i) RGO/AuNP and (ii) GO/AuNP.

[0016] **Figure 5** is a series of images showing (A) optical image of multilayer AuNP/RGO hybrid film on the indium tin oxide (ITO) substrate; (B) cross-section scanning electron microscopy (SEM) image of multilayer AuNP/GO hybrid film; (C) SEM image of the fracture edge of the multi-layered hybrid film; (D) SEM image of a compact RGO film i.e. RGO film without AuNP interlayer, taken of the edge of the film; (E) SEM image of the cross-section of a multilayer RGO/AuNP hybrid film. The inset of (E) is an SEM image of AuNPs on the graphene sheet surface. The scale bar in **Figure 5B** denotes 4 μm ; **Figure 5C**: 300 nm; **Figure 5D**: 500 nm; **Figure 5E**: 4 μm . The scale bar in the inset image of **Figure 5E** denotes a length of 300 nm.

30 [0017] **Figure 6** is a SEM image of compact RGO film i.e. RGO film without AuNP interlayer, taken of the edge of the film.

[0018] **Figure 7** is a graph showing effect of the deposition time of AuNP on the sheet resistances and AuNP densities of multilayer RGO/AuNP films.

[0019] **Figure 8** are optical images of a process of transferring a RGO/AuNP hybrid film from ITO surface to other substrates. (A) Optical image of a multilayer RGO/AuNP hybrid film on ITO substrate; (B) Optical image of the hybrid film on water surface; (C) Optical image of the hybrid film on PET substrate.

[0020] **Figure 9** is a schematic diagram depicting a process of transferring a RGO/AuNP hybrid film from ITO surface to other substrates. (A) A multilayer RGO/AuNP film on a ITO substrate; (B) free-standing RGO/AuNP multilayer film after removal of ITO substrate; (C) transfer of the multilayer RGO/AuNP film on a PET substrate.

[0021] **Figure 10** is (A) schematic diagram, and (B) optical image of the flexible multilayered AuNP/RGO hybrid film supercapacitor using free-standing SWCNT film as current collector.

[0022] **Figure 11** is a series of images showing (A) optical image, and (B) SEM image of directly grown single-walled carbon nanotube (SWCNT) film. It can be seen from **Figure 11B** that the SWCNT film is porous and composed of highly entangled SWCNT bundles. The scale bar in **Figure 11B** denotes a length of 400 nm.

[0023] **Figure 12** is a series of graphs showing (A) cyclic voltammetry (CV) curves of the representative supercapacitors using (i) pure RGO film without SWCNT film current collector, (ii) RGO/SWCNT film, and (iii) AuNP/RGO/SWCNT film, as electrodes; (B) the CVs normalized to 1; (C) the CV curves of a representative AuNP/RGO film electrode supercapacitor at different scan rates; and (D) the specific capacitance of AuNP/RGO film supercapacitors as a function of AuNP deposition time.

[0024] **Figure 13** is a graph showing typical galvanostatic charge/discharge curves of the representative multilayer hybrid film supercapacitor at 1 A/g.

[0025] **Figure 14** is (A) a graph showing the specific capacitance of the AuNP/RGO film supercapacitors with different deposition time at different scan rate; and (B) the graph with values normalized to 1.

[0026] **Figure 15** is a series of graphs depicting the CVs of (A) RGO film, and (B) Au/RGO hybrid film electrodes in 0.5 M potassium chloride (KCl) solution in presence of 10 mM potassium ferrocyanide ($K_4[Fe(CN)_6]$) and potassium ferricyanide ($K_3[Fe(CN)_6]$) at

different scan rates; (C) anodic and cathodic peaks as a function of the square root of the scan rate.

[0027] **Figure 16** is a schematic diagram of fabricating RGO/AuNP lateral pattern by electrophoretic buildup. A: a layer of photoresist is coated on a suitable substrate; B: the photoresist is patterned using a patterning method such as photolithography; C: a multilayer GO/AuNP film is deposited on the unpatterned portions of the substrate using electrophoretic deposition; D: the multilayer GO/AuNP film is reduced to form RGO/AuNP multilayers; E: photoresist is removed.

[0028] **Figure 17** is (A) an optical microscope image; and (B) scanning electron microscopy (SEM) image of a multilayer RGO/AuNPs structure comprising two layers of RGO and two layers of AuNPs square patterns. The scale bar in each of **Figures 17A** and **17B** denotes a length of 100 μm .

[0029] **Figure 18** is (A) an optical microscope image; (B) scanning electron microscopy (SEM) image of multilayer RGO/AuNP stripe patterns comprising two layers of RGO and two layers of AuNPs at low magnification; (C) SEM image of (B) at high magnification. The scale bar in each of **Figures 18A** and **18B** denotes a length of 200 μm . The scale bar in **Figure 18C** denotes a length of 200 nm.

DETAILED DESCRIPTION OF THE INVENTION

[0030] In a first aspect, the present invention refers to a method of the preparation of a multilayer film comprising metal nanoparticles and a graphene-based material using electrophoretic deposition.

[0031] Electrophoretic deposition, as defined herein, refers to a process in which charged particles that are solved, dispersed within or suspended in a liquid medium are driven towards an oppositely charged electrode under application of an electric field, thereby depositing or coating the particles on the electrode. The term "particles" as used herein also refers to colloidal particles, macromolecules, molecules, or ions. Depending on the type of particles used, the particles may be present in the liquid medium as a suspension, a colloidal dispersion, or a solution. Generally, any material that can be solved, dispersed within or suspended in a liquid medium, and which can carry a charge may be used to form particles for electrophoretic deposition. The particles may be deposited on the cathode or the anode, depending on the type of charge that is present on the particles. When positively charged

particles are used, for example, the particles are deposited on the cathode i.e. the negatively charged electrode. Conversely, when negatively charged particles are used, the particles are deposited on the anode i.e. the positively charged electrode.

[0032] Using a method of the present invention, a multilayer film comprising alternating layers of metal nanoparticles and a graphene-based material may be formed. In various embodiments, the metal nanoparticles and the graphene-based material are negatively charged, and are coated in alternate layers on the anode to form a multilayer film. The anode may comprise a substrate onto which deposition of the particles is desired. The substrate may, in general, be formed from any conductive material. For example, the substrate may be a metal such as a noble metal or a transition metal, a conductive polymer, or carbon such as graphene. Examples of a noble metal include silver (Ag), palladium (Pd), gold (Au), platinum (Pt), iridium (Ir), osmium (Os), rhodium (Rh) and ruthenium (Ru). Examples of a transition metal include titanium (Ti), vanadium (V), chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu) and zinc (Zn). Examples of a conductive polymer include polypyrrole and its derivatives and copolymers; polythiophene and its derivatives and copolymers, including poly(3-alkyl thiophenes) and poly(3,4-ethylenedioxythiophene) (PEDOT); polyaniline and its derivatives and copolymers; poly(p-phenylene vinylene) and its derivatives and copolymers; polysulfone and its derivatives and copolymers; and polyacetylene and its derivatives and copolymers.

[0033] In various embodiments, a non-conductive material having a coating of a conductive material may also be used as the substrate. For example, the substrate may be glass having a layer of metal coated thereon. In one embodiment, the substrate is indium tin oxide (ITO) coated glass.

[0034] The method of the present invention includes electrophoretically depositing a layer of graphene-based material on a substrate. In various embodiments, the graphene-based material is graphene oxide, which is a layered material derived from the oxidation of graphite, and can be visualized as a graphene sheet with its basal plane decorated by oxygen-containing groups such as carboxyls, epoxides and alcohols.

[0035] The method to form the first layer of graphene-based material on the substrate using electrophoretic deposition may include dispersing the graphene-based material in a liquid medium to form a suspension. In various embodiments, the graphene-based material may be homogeneously dispersed within the liquid medium. For example, when graphene

oxide is used, due to the presence of oxygen-containing groups, graphene oxide is hydrophilic, and can be dispersed readily into individual sheets of graphene oxide in a suitable liquid medium. The choice of a liquid medium may depend on factors such as conductivity of the liquid medium and its ability to wet the particles in suspension. A suitable liquid medium may, for example, be one that has a high dielectric constant and is able to wet the particles in suspension well. In various embodiments, the liquid medium is an organic solvent. Organic solvents that are generally polar, such as alcohols and ketones, may be used. Examples of organic solvents that may be used include dimethylformamide, ethanol, acetone, and methyl ethyl ketone, to name a few. Alternatively, the liquid medium may be an aqueous medium, such as water. In one embodiment, the liquid medium is dimethylformamide, to which graphene oxide is added to form a graphene oxide-dimethylformamide (GO-DMF) suspension.

[0036] Mechanical stirring or ultrasonication may optionally be used to disperse the graphene-based material within the liquid medium. In some embodiments, the suspension comprising the graphene-based material may be subjected to centrifugation to remove any aggregates of the graphene-based material, with this additional step being carried out to achieve a more uniform deposition of the graphene-based material.

[0037] Upon formation of the suspension, the suspension may be contacted with two electrodes to which an electrical voltage is applied. In various embodiments, the graphene-based material is negatively charged, and is deposited on the positive electrode or anode. The positive electrode may comprise the substrate onto which deposition of the particles is desired. For example, when the graphene-based material comprises negatively charged graphene oxide particles, the positive electrode or anode may be formed from indium tin oxide (ITO) coated glass. A voltage may be applied to the electrodes such that the graphene-based material is deposited on the substrate. The magnitude of voltage to be used may depend on the material for deposition and the liquid medium used. In various embodiments, the applied voltage is about 15 V to about 50 V, for example about 30 V.

[0038] The method of generating a multilayer film comprising metal nanoparticles and a graphene-based material using electrophoretic deposition comprises forming a layer of metal nanoparticles on the layer of graphene-based material that is deposited on the substrate. Metals that may be used to form the metal nanoparticles include noble metals, transition metals and their alloys. Examples of noble metals and transition metals have already been

described herein. Other examples of metal that may be used include rare earth metals such as scandium (Sc), yttrium (Y), lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb) and lutetium (Lu); and metalloids such as boron (B), silicon (Si), germanium (Ge), arsenic (As), antimony (Sb), and tellurium (Te); and their alloys. In various embodiments, the metal nanoparticles comprise a noble metal selected from the group consisting of gold, silver, platinum, iridium, ruthenium, rhodium and palladium. In one embodiment, the metal nanoparticles are gold nanoparticles.

[0039] The method of forming the layer of metal nanoparticles on the layer of graphene-based material may include preparing a suspension comprising the metal nanoparticles. For example, the suspension comprising the metal nanoparticles may be formed by mixing metal nanoparticles in a non-solvent or in a liquid medium which does not chemically react with the metal nanoparticles. In various embodiments, the metal nanoparticles form a stable colloidal dispersion. In embodiments in which gold nanoparticles are used, citrate-stabilized gold nanoparticles may be prepared by thermal reduction of chloroauric acid (HAuCl_4) with sodium citrate (see, Example 2), with subsequent dispersion of the gold nanoparticles in a liquid medium such as dimethylformamide to form the suspension.

[0040] The metal nanoparticles may be negatively charged. The negative charge on the metal nanoparticles may function to avoid aggregation of the metal nanoparticles in suspension, and to allow the movement of the metal nanoparticles to the positive electrode during electrophoretic deposition. Metal nanoparticles with a negative charge may be nanoparticles wherein the negative charge of the metal nanoparticles is conferred by a carboxylic acid or sulfonic acid or carboic acid or a mixture of the aforementioned acids which is/are immobilized on the surface of the metal nanoparticles. In one embodiment, the carboxylic acid can be, but is not limited to citric acid, lactic acid, acetic acid, formic acid, oxalic acid, uric acid, pyrenedodecanoic acid, mercaptosuccinic acid, aspartic acid, to name only a few. In the case of citrate-stabilized gold nanoparticles, which may be prepared by thermal reduction of chloroauric acid (HAuCl_4) with sodium citrate, the surface of the nanoparticles may be rendered negatively charged as a result of citrate ions which are immobilized on the surface of the nanoparticles. In various embodiments, the citrate ions form a layer on the surface of the gold nanoparticles.

[0041] The suspension comprising the metal nanoparticles may be contacted with two electrodes to which an electrical voltage is applied. The positive electrode i.e. anode may comprise the substrate having the layer of graphene-based material deposited thereon, such that when a voltage is applied to the electrodes, the metal nanoparticles are deposited on the layer of graphene-based material.

[0042] The metal nanoparticles may be irregular or regular in shape. In some embodiments, the metal nanoparticles are regular in shape. For example, the metal nanoparticles may have a regular shape such as a sphere, a cube or a tetrahedron. Accordingly, the metal nanoparticles may otherwise be referred to as metal nanospheres, metal nanocubes, or metal tetrahedra.

[0043] The size of the metal nanoparticles may be characterized by their mean diameter. The term "diameter" as used herein refers to the maximal length of a straight line segment passing through the center of a figure and terminating at the periphery. The term "mean diameter" refers to an average diameter of the nanoparticles, and may be calculated by dividing the sum of the diameter of each nanoparticle by the total number of nanoparticles. Although the term "diameter" is used normally to refer to the maximal length of a line segment passing through the centre and connecting two points on the periphery of a nanosphere, it is also used herein to refer to the maximal length of a line segment passing through the centre and connecting two points on the periphery of nanoparticles having other shapes, such as a nanocube or a nanotetrahedra. In various embodiments, the metal nanoparticles may have a mean diameter of less than 100 nm, such as in a range of about 10 nm to about 90 nm, or in a range of about 10 nm to 50 nm. In another example, the size of the nanoparticles is in range of between about 10 nm to 30 nm, or about 20 nm to 30 nm. The metal nanoparticles may be essentially monodisperse to form a substantially homogeneous layer of metal nanoparticles during electrophoretic deposition.

[0044] In embodiments where the metal nanoparticles are gold nanoparticles, the electrophoretic deposition of the gold nanoparticles is carried out for a time period ranging from about 100 seconds to about 150 seconds, such as about 100 seconds, about 120 seconds, or about 140 seconds. In one embodiment, the electrophoretic deposition of the gold nanoparticles is carried out for about 120 seconds, which has been found by the inventors of the present invention to form an optimal density of gold nanoparticles layer on a graphene oxide-layer.

[0045] The method of generating a multilayer film comprising metal nanoparticles and a graphene-based material using electrophoretic deposition includes optionally repeating the steps of electrophoretically depositing the layer of graphene-based material and the layer of metal nanoparticles for one or more additional cycles, for example for 1, 2, 3, 4, 5, 6, 7, 8, 9, 10 or more additional cycles. By repeating the above-mentioned processes for forming the layer of graphene-based material and the layer of metal nanoparticles, a multilayer film comprising alternating layers of the graphene-based material and the metal nanoparticles may be obtained.

[0046] The method of the present invention further comprises forming a layer of graphene-based material on the layer of metal nanoparticles. For example, the method of forming the layer of graphene-based material on the layer of metal nanoparticles may comprise preparing a suspension comprising the graphene-based material, and contacting two electrodes with the suspension, wherein the anode comprises the substrate having the layer of metal nanoparticles deposited thereon, such that when a voltage is applied to the electrodes, the graphene-based material is deposited on the layer of metal nanoparticles. In various embodiments, the step of depositing a layer of graphene-based material on the layer of metal nanoparticles may be carried out similar to the first step of depositing a layer of graphene-based material, as described above.

[0047] Even though it has been described herein that the layer of graphene-based material is deposited on the substrate, with subsequent deposition of the layer of metal nanoparticles on the layer of graphene-based material, the layer of metal nanoparticles may alternatively be electrophoretically deposited on the substrate, with subsequent electrophoretic deposition of the layer of graphene-based material on the layer of metal nanoparticles.

[0048] The multilayer film comprising the metal nanoparticles and the graphene-based material may be contacted with a reducing agent. The term "reducing agent" as used herein, refers to an agent that donates electrons in an oxidation-reduction reaction. Examples of a reducing agent include, but are not limited to, a hydrazine compound, hydrogen, formaldehyde, and hydroxylamine. For example, the reducing agent may be a hydrazine compound containing a hydrazino-group. Examples of a hydrazine compound that may be used include hydrazine, hydrazine hydrochloride, hydrazine sulfate, hydrazine hydrate, hydrazine monohydrate, phenyl hydrazine, benzyl hydrazine, and ethyl hydrazine. In one embodiment, the reducing agent is hydrazine monohydrate. In embodiments in which the

graphene-based material is graphene oxide, for example, the reducing agent may be used to reduce graphene oxide (GO) to form reduced graphene oxide (RGO), or graphene. In so doing, the insulating graphene oxide may be converted to reduced graphene oxide, which is conductive.

5 [0049] The method of generating a multilayer film comprising metal nanoparticles and a graphene-based material using electrophoretic deposition may further comprise removing the multilayer film from the substrate. For example, a rigid material such as ITO coated glass may be used as the substrate to facilitate processing during electrophoretic deposition. For subsequent use of the multilayer film in flexible devices for example, it may be necessary to
10 transfer the multilayer film to a flexible substrate, such as polyethylene terephthalate (PET). In various embodiments, the multilayer film is separated from the substrate by immersing the substrate comprising the multilayer film in an aqueous medium, such as water. In doing so, the aqueous medium may migrate into the interface between the substrate and the multilayer film to separate the two. As a result, a free-standing multilayer film may be obtained. The
15 free-standing multilayer film may be transferred to another substrate for subsequent processing or for use in applications.

[0050] Besides forming the multilayer film on a planar surface as described above, the method of generating a multilayer film comprising metal nanoparticles and a graphene-based material using electrophoretic deposition may also be carried out using a substrate that is
20 patterned with a photoresist. As a result, a patterned multilayer film comprising metal nanoparticles and a graphene-based material may be obtained. Non-limiting examples of photoresist include 1-Methoxy-2-propanol acetate (SU-8), bisazides, poly(vinyl cinnamate), novolak (M-Cresol-formaldehyde), polymethylmethacrylate (PMMA), photo sensitive polyimide and epoxy. In various embodiments of the invention, the photoresist is SU-8. The
25 photoresist may be coated or formed on a substrate using any deposition method, such as painting, spin coating or dip coating. State of the art patterning methods, such as photolithography or nanoimprint lithography may be used to pattern the photoresist. The photoresist may be formed from a non-conducting material, such that when the resultant patterned substrate is used in electrophoretic deposition according to a method of the
30 invention, the multilayer film is deposited on the unpatterned portions of the substrate, corresponding to areas on the substrate which are not coated with the photoresist (see, Example 10). The multilayer film may optionally be contacted with a reducing agent such as

hydrazine monohydrate, with subsequent removal of the resist using a suitable solvent, such as acetone, to result in the patterned multilayer film.

[0051] In a second aspect, the invention refers to a multilayer film comprising metal nanoparticles and a graphene-based material obtainable by a method of the first aspect. In a further aspect, the invention refers to a multilayer film comprising a layer of metal nanoparticles between a first layer of a graphene-based material and a second layer of a graphene-based material.

[0052] As used herein, the term "multilayer film" refers to a structure having two or more layers of a film. The multilayer film according to various embodiments of the invention is formed using electrophoretic deposition. In various embodiments, the graphene-based material is graphene oxide or reduced graphene oxide. Suitable materials that may be used as the metal nanoparticles of the multilayer film have already been described above.

[0053] The thickness of the first layer and the second layer of the graphene-based material may be the same or different, and may depend on the requirements of the specific application in which the multilayer film is used. Generally, the thickness of the first layer and the second layer of the graphene-based material may be controlled by the duration of electrophoretic deposition. The duration required to achieve a specific thickness of electrophoretic deposition may in turn be affected by factors, such as the concentration of the graphene-based material in the liquid medium, the type of graphene-based material used, and/or the type of liquid medium in which the graphene-based material is dispersed in.

[0054] Similarly, the thickness of the layer of metal nanoparticles may also depend on the requirements of the specific application in which the multilayer film is used, and may be controlled by varying the duration of electrophoretic deposition, for example. In various embodiments, the metal nanoparticles are deposited as a monolayer on the graphene-based material. Therefore, the thickness of the layer of metal nanoparticles may correspond to the mean diameter of the metal nanoparticles.

[0055] The density of the layer of metal nanoparticles may be about $150 \mu\text{m}^{-2}$ to about $450 \mu\text{m}^{-2}$, such as about $150 \mu\text{m}^{-2}$ to about $300 \mu\text{m}^{-2}$, or about $200 \mu\text{m}^{-2}$.

[0056] In various embodiments in which the graphene-based material is reduced graphene oxide, the layer of metal nanoparticles may form a homogeneous layer between the first layer and the second layer of reduced graphene oxide. By forming the homogeneous metal nanoparticles layer, the bridging effect of the metal nanoparticles between the layers of the

reduced graphene oxide may be enhanced, which may in turn result in an improved electrical conductivity of the multilayer structure.

[0057] In a fourth aspect, the invention refers to an electrode comprising a multilayer film according to the second or the third aspect, wherein the graphene-based material is reduced graphene oxide. In various embodiments, the electrode is an electrode comprised in a supercapacitor, a sensor, a hybrid electrochemical device, a rechargeable battery, or a metal-air battery.

[0058] By forming the multilayer film using electrophoretic deposition, the nano-architecture of the multilayer film comprising graphene-based material and metal nanoparticles along the normal direction of the film, such as the number and thickness of the layers, may be controlled easily. Furthermore, lateral orientation of the multilayer film may be customized easily through the use of a patterned substrate. Conductivity of a multilayer hybrid nano-architecture generated according to various embodiments of the invention has shown significant improvement which may be attributed to bridging effect of metal nanoparticles along the out-of-plane direction between the upper and lower layers of a graphene-based material. As a result, a transparent, ultrathin hybrid film may be prepared using a method of the invention.

[0059] Furthermore, the multilayer films according to various embodiments of the invention do not require the use of a binder or an additive. This means that the performance of the films would not be negatively impacted through the use of any insulating binder or a low capacitance conducting additive.

[0060] The multilayer metal nanoparticles/graphene-based material film with enhanced active surface area may be used, for example, as electrode material for supercapacitors, lithium batteries, biosensors and gas sensors. For example, it has been demonstrated herein that a multilayer film comprising reduced graphene oxide and gold nanoparticles according to various embodiments of the invention can be used as electrodes in flexible supercapacitors, and excellent performance, such as high energy and power densities, have been achieved. These results clearly illustrate the potential of electrophoretic buildup in the fabrication of graphene-based alternating multilayer films and lateral patterns. Besides its use as an electrode material in supercapacitors, batteries, and sensors, the ultrathin hybrid film may also be used in the manufacture of transparent or semi-transparent film electrodes in solar

energy conversion devices, as well as substrate for surface enhanced resonance spectroscopy (SERS).

[0061] The invention illustratively described herein may suitably be practiced in the absence of any element or elements, limitation or limitations, not specifically disclosed herein. Thus, for example, the terms "comprising", "including", "containing", etc. shall be read expansively and without limitation. Additionally, the terms and expressions employed herein have been used as terms of description and not of limitation, and there is no intention in the use of such terms and expressions of excluding any equivalents of the features shown and described or portions thereof, but it is recognized that various modifications are possible within the scope of the invention claimed. Thus, it should be understood that although the present invention has been specifically disclosed by preferred embodiments and optional features, modification and variation of the inventions embodied therein herein disclosed may be resorted to by those skilled in the art, and that such modifications and variations are considered to be within the scope of this invention.

[0062] The invention has been described broadly and generically herein. Each of the narrower species and subgeneric groupings falling within the generic disclosure also form part of the invention. This includes the generic description of the invention with a proviso or negative limitation removing any subject matter from the genus, regardless of whether or not the excised material is specifically recited herein.

[0063] Other embodiments are within the following claims and non-limiting examples. In addition, where features or aspects of the invention are described in terms of Markush groups, those skilled in the art will recognize that the invention is also thereby described in terms of any individual member or subgroup of members of the Markush group.

EXPERIMENTAL SECTION

[0064] **Figure 1A** is a schematic diagram showing electrophoretic deposition of (I) a graphene-based material, and (II) metal nanoparticles in an electrophoretic cell. These two steps form the basic buildup sequence for the architecture of the multilayer graphene-based material/metal nanoparticles composite films. As shown in **Figure 1A(I)**, a negative electrode and a positive electrode comprising a suitable substrate are inserted into a suspension comprising a graphene-based material. A voltage is applied to the electrodes to coat the negatively-charged graphene-based material on the substrate. Subsequently, as

shown in **Figure 1A(II)**, the negative electrode and the substrate comprising the negatively charged graphene-based material, which acts as the positive electrode, are inserted into a suspension comprising metal nanoparticles. A voltage is applied to the electrodes to coat the negatively charged metal nanoparticles on the graphene-based material on the substrate.

5 [0065] **Figure 1B** is a schematic diagram showing electrophoretic deposition of (I) graphene oxide (GO), and (II) gold nanoparticles (AuNPs) according to various embodiments of the invention. Platinum was used as the negative electrode, and indium tin oxide (ITO) coated glass substrate was used as the positive electrode. In this embodiment, the electrostatic force is the driving force of electrophoresis for depositing GO sheets or AuNPs onto
10 substrate, in which the applied electric field drives charged GO nanosheets and AuNPs toward a field-emanating surface. Therefore, when the electric field (2 kV/m to GO sheets, 3 kV/m to AuNPs) was applied, the negatively charged GO sheets in DMF solution or AuNPs in DMF solution (**Figure 3**) migrated to the anode (indium tin oxide (ITO) glass) and subsequently formed a layer of film on it. Therefore, alternately multilayer GO/AuNP films
15 could be constructed on the conductive electrode by repeating GO and AuNP deposition processes consecutively

[0066] Exemplary processes are described in the following examples.

[0067] **Example 1: Fabrication of Graphene Oxide-Dimethylformamide (GO-DMF) suspension**

20 [0068] The GO colloidal suspension was prepared using the procedure outlined below. Briefly, 1.5 g graphite was added to 35 ml concentrated sulfuric acid at room temperature under stirring. Under vigorous agitation, 0.75 g sodium nitrate and 4.5 g potassium permanganate were added respectively to the mixture at 0 °C in a slow manner.

[0069] Subsequently, the mixture was heated to 35 °C to 40 °C in a water bath for about
25 0.5 hours to form a thick paste. 70 ml water was then added, and the solution was stirred for another 15 minutes. An additional 250 ml of water was added, followed by a slow addition of 10 ml of hydrogen peroxide (H₂O₂) (30%), whereupon addition of the hydrogen peroxide, the color of the solution changed from brown to yellow.

[0070] The mixture was filtered and washed with 125 ml of an hydrochloric acid (HCl)
30 aqueous solution (1:10) to remove metal ions, followed by repeated washing with water and centrifugation to remove the acid. The resulting solid was dispersed in water by ultrasonication for 5 hours to make a GO-aqueous suspension, which was then subjected to 30

minutes of centrifugation at 5000 rpm or 7000 rpm to remove the aggregates. Subsequently, it was purified by dialysis to remove the remaining salt impurities.

[0071] The GO colloidal suspension was dried at 40 °C. The resulting GO powder was dispersed into dimethylformamide (DMF) by ultrasonication for 5 hours to obtain a GO-DMF suspension. The GO-DMF suspension was then centrifuged for 30 min at 5000 rpm to remove the aggregates. Finally, the GO-DMF suspension was obtained as shown in **Figure 3A**.

[0072] **Example 2: Fabrication of gold-dimethylformamide (AuNP-DMF) suspension**

[0073] Gold nanoparticles (AuNPs) were prepared by sodium citrate reduction of a chloroauric acid (HAuCl₄) to form a gold colloidal solution. The gold colloidal solution was centrifuged for 15 minutes at 10000 rpm. The resulting solid was dispersed into DMF, and a AuNP-DMF suspension was obtained as shown in **Figure 3B**.

[0074] **Example 3: Preparation of multilayer hybrid film by electrophoretic method**

[0075] GO and AuNP layers were constructed by electrophoretic method in a two-electrode system, and ITO glass substrate and a platinum plate were used as positive and negative electrodes, respectively.

[0076] **Example 3.1: Deposition of GO film**

[0077] Before depositing GO film, the indium tin oxide (ITO) was treated by argon plasma for 10 min. For the deposition of GO layers, GO DMF suspension (0.5 mg/ml) was used as the electrolyte, as shown in **Figure 1B (I)**. The distance between the two electrodes was 1.5 cm, and the applied voltage was 30 V. Under the applied voltage, the negatively charged GO sheets migrated towards the positive electrode, and were subsequently orderly deposited onto the conducting substrate. The GO deposition time was 240 s

[0078] **Example 3.2: Deposition of gold nanoparticles layer**

[0079] The platinum plate was used as negative electrode, and the conducting ITO substrate with GO film coating was used as positive electrode, as shown in **Figure 1B (II)**. The AuNP-DMF suspension was used as the electrolyte. The distance between the two electrodes was 1 cm and the applied voltage was 30 V.

[0080] **Example 3.3: Formation of multilayer AuNP/GO hybrid film structure**

[0081] Multilayer AuNP/GO hybrid films with a specific number of layers and thickness on a conducting substrate may be fabricated by repeated iterations of the electrophoretic

deposition processes shown in **Figure 1B**. The area of the multi-layered hybrid film may be scaled up by increasing the area of conducting positive electrode.

[0082] Example 3.4: Reduction of multilayer AuNP/GO hybrid film

[0083] **Figure 2** is a series of schematic diagrams depicting the formation of multilayer RGO/AuNP film, and subsequent chemical reduction of the multilayer GO/AuNP film to RGO/AuNP film according to embodiments of the invention. (A) A first layer of graphene oxide is coated on an ITO coated glass substrate; (B) a layer of gold nanoparticles is coated on the graphene oxide; (C) a second layer of graphene oxide is coated on the layer of gold nanoparticles; (D) the multilayer GO/AuNP film is chemically reduced to RGO/AuNP film using a reducing agent such as hydrazine monohydrate.

[0084] The multilayer GO-based hybrid film formed was chemically reduced using hydrazine monohydrate (98 %) at 90 °C to obtain a multilayer AuNP/RGO hybrid film (refer to **Figure 2D**).

[0085] Raman spectrum can reflect the significant structural changes during the chemical process from GO to RGO. Referring to **Figure 4**, the intensity ratio $I(D)/I(G)$ of RGO/AuNP films is slightly increased in comparison with that of GO/AuNP film. This change is attributed to the increased defect concentration existed in RGO relative to that in GO and the numerous new graphene domains that were created during the chemical process from GO to RGO.

[0086] Example 4: Characterization of multilayer AuNP/RGO hybrid film

[0087] Example 4.1: Analytical equipment used

[0088] The morphology and the microstructures of multilayer hybrid film and the SWCNT films were characterized by FE-SEM (Hitach S-5200 and JSM-7600F). The sheet resistance of the multilayer hybrid film was measured by Fluke 179 True RMS Multimeter. The Raman spectra were obtained with spectrophotometer (WITec alpha 300 R). The operating wavelength was 633 nm.

[0089] Example 4.2: Optical and scanning electron microscopy images

[0090] **Figure 5A** shows the optical image of multilayer AuNP/RGO hybrid film on the indium tin oxide (ITO) substrate. **Figure 5B** is the cross-section scanning electron microscopy (SEM) image of multilayer AuNP/GO hybrid film. **Figure 5B** reveals that Au NPs are sandwiched between RGO layers. The layer-by-layer structure can also be observed from the SEM image of the fracture edge of the multi-layered hybrid film, as shown in

Figure 5C. It is evident that the RGO nanosheets could uniformly cover the dispersed AuNPs. The RGO nanosheets interact with the AuNPs through the large basal plane area, and at the same time, the large RGO nanosheets are also connected with each other and form the RGO layers on the top of AuNP layers. However, the upper RGO layer and lower RGO layer of AuNPs layer are separated by the AuNPs layer and could not connect with each other.

[0091] **Figure 5E** is a scanning electron microscopy (SEM) image of the cross-section of a multilayer RGO/AuNP hybrid film where AuNPs are sandwiched between RGO layers. AuNPs are homogeneously dispersed onto RGO surface, as shown in the inset of **Figure 5E**. In multilayer RGO/AuNP hybrid films, the graphene nanosheets interact with AuNPs through the large basal plane area, and at the same time the large graphene nanosheets are also connected with each other and form the RGO layers on the top of AuNP layers. Significantly, the upper and lower RGO layers are separated by AuNP layers and could be not restacked with each other, which is different with the pure RGO film with compact structures (see **Figure 6**). **Figure 6** is a SEM image of compact RGO film i.e. RGO film without AuNP interlayer, taken of the edge of the film. AuNP layers in multilayer RGO/AuNP hybrid structures may provide effective diffusion channels for ion transportation, and form conductive bridge between RGO layers, which is of great significance for its potential applications, such as electrochemical electrodes.

[0092] The fabrication of multi-layered hybrid nano-architecture by electrophoretic deposition could control the structure of hybrid film easily, including the layers and thickness of single RGO and AuNP layer. In this multi-layered hybrid nano-architecture, Au nanoparticle layers provide a support for the RGO layers and avoid the self-aggregation of RGO layers. It increases the space between RGO layers and improves the active surface area of RGO compared with that of the compact RGO film, which refers to a multilayer RGO film having no AuNP interlayer, prepared under the same conditions (**Figure 5D**), which is of great significance for the applications of RGO, such as electrochemical electrodes and sensors.

[0093] Furthermore, GO nanosheets resulting from chemical exfoliation of graphite comprise negatively charged colloidal particles by a variety of oxygen containing groups (zeta potential of -45 mV), while AuNPs prepared by sodium citrate reduction are also negatively charged (zeta potential of -25 mV). Therefore, processes such as alternate

adsorption of polyanions and polycations cannot be used to obtain the multilayer GO/AuNPs film.

[0094] Example 4.3: Conductivity

[0095] The high conductivity of hybrid film was achieved due to connection of AuNPs with high conductivity between RGO layers, as shown in **Figure 7**. **Figure 7** is a graph showing effect of the deposition time of AuNP on the sheet resistances and AuNP densities of multilayer RGO/AuNP films. It shows that the sheet resistance of the hybrid film was decreased with the increase of AuNP deposition time, and with an increase in the density of the AuNPs. The conductivity of hybrid film with 180 seconds of AuNP deposition time is about twice of that for the compact RGO film.

[0096] Referring to **Figure 7**, with the increase in AuNP deposition time, more AuNPs would migrate to positive electrode and the AuNP density on multilayer GO/AuNP hybrid films would be increased. As conductive bridges, more AuNPs sandwiched between RGO layers would bring lower resistance along the out-of-plane direction between the upper and lower layers of the RGO layers. Therefore, the sheet resistance of the RGO/AuNP hybrid film decreases with an increase in AuNP deposition time. It indicates that conductivity of multilayer RGO/AuNP hybrid nano-architecture shows great improvement caused by a bridging effect of AuNPs along the out-of-plane direction between the upper and lower layers of the RGO layers. Therefore, in the multilayer RGO/AuNP hybrid nano-architecture, not only does the AuNP layer prevent the self-agglomeration of RGO sheets, it also connects the RGO layers well.

[0097] Example 5: Transfer of multilayer AuNP/GO hybrid film to flexible substrate

[0098] To meet the requirement of flexible devices, the multilayer AuNP/RGO hybrid film on the substrates that is not flexible, such as ITO substrate, has to be transferred to other flexible substrates. **Figure 8** are optical images of a process of transferring a RGO/AuNP hybrid film from ITO surface to other substrates. (A) Optical image of a multilayer RGO/AuNP hybrid film on ITO substrate; (B) Optical image of the hybrid film on water surface; (C) Optical image of the hybrid film on PET substrate. **Figure 9** is a schematic diagram depicting a process of transferring a RGO/AuNP hybrid film from ITO surface to other substrates. (A) A multilayer RGO/AuNP film on a ITO substrate; (B) free-standing RGO/AuNP multilayer film after removal of ITO substrate; (C) transfer of the multilayer RGO/AuNP film on a PET-substrate.—

[00099] The multilayer reduced graphene hybrid film was put into water at about 90 °C for several hours, after which it may be peeled from ITO glass at about 80 °C, where the hybrid film can either be peeled from the inflexible substrate or may float on the surface of water. Then free-standing the hybrid film can be transferred onto other substrates for applications.

5 [00100] Since the ITO surface treated by argon plasma was hydrophilic because of the existence of hydrophilic groups and the surface of the RGO/AuNP hybrid films was hydrophobic, water may slowly migrate into the interface between ITO and the RGO/AuNP hybrid films to separate them. Experimentally, it clearly showed that the RGO/AuNP hybrid film was free-floating on the surface of water (as shown in **Figure 8B**), which brings the
10 convenience for further transferring the hybrid film to other substrates, such as flexible PET substrate (as shown in **Figure 8C**).

[00101] Before peeling from ITO, the hybrid film can be tailored into desired shapes easily according to the demands of the designed devices. After peeling from ITO, the hybrid film with designed shape can be obtained and transferred to other substrates. It is also noted that
15 the addition of AuNPs has little effect on the flexibility of the multilayer RGO/AuNP hybrid films. The flexibility of hybrid film also provide the possibility of directly shaping the film into desired structures by convenient techniques, such as using a cutter, even when the hybrid film has been transferred to other flexible substrates.

[00102] **Example 6: Fabrication and characterization of flexible multilayer film**
20 **supercapacitors**

[00103] Since the hybrid films with multi-layered nano-architecture have higher active electrochemical surface area and conductivity, the hybrid films can be used for fabricating supercapacitor devices, and neither an insulating binder nor a low capacitance conducting additive is required. In traditional supercapacitors, metallic current collectors (metallic foils
25 or foams) were normally used as electrode materials for both anode and cathode in the supercapacitor devices due to their poor conductivity. However, use of metallic current collectors will make the supercapacitors too heavy or bulky, which will limit use of the supercapacitors in the applications that are limited in space and weight.

[00104] Single-walled carbon nanotube (SWCNT) films were used as charge collectors
30 instead of metallic foils or foams, because SWCNTs have high conductivity, low mass density, large specific surface area and high mechanical strength. Although specific capacitance of the SWCNT film supercapacitors was generally small, because the SWCNTs

normally exist in form of bundles, which reduce its active electrochemical surface area, the significantly high conductivity of SWCNT film makes it possible for SWCNTs to be used as current collectors.

[00105] Compared to metallic current collectors, SWCNT film has many advantages for use as current collectors: 1) Not only can SWCNT films be used as current collectors, they can also provide capacitance. Metallic foils or foams, on the other hand, can be only used as current collectors and have no contribution to the capacitance. 2) The thickness of freestanding SWCNT film used as current collectors can be about several hundred nanometers, even 100 nm. Besides, the mass density of SWCNT film is much smaller than that of metallic current collectors. These are of great significance for the supercapacitors that are limited in space and weight. 3) The porous property of SWCNT films may be useful to improve the penetration of electrolytic ions into the electrodes, leading to a high specific capacitance.

[00106] **Figure 10A** is a schematic diagram of the flexible multi-layered AuNP/RGO hybrid film supercapacitor using free-standing SWCNT film as current collector. The SWCNT films were directly fabricated by floating catalyst chemical vapour deposition (CVD) (shown in **Figure 11**). **Figure 11** is a series of images showing (A) optical image, and (B) SEM image of directly grown SWCNT film. It can be seen from **Figure 11B** that the SWCNT film is porous and composed of highly entangled SWCNT bundles.

[00107] The directly prepared SWCNT films with about 150 nm thickness were first uniformly spread out onto polyethylene terephthalate (PET) in ethanol as current collector. After the ethanol was evaporated, the SWCNT film can adhere firmly to the PET substrate due to the self-adhesion of the SWCNT film. The multi-layered AuNP/GO hybrid film was then transferred to the surface of SWCNT film on the PET. Celgard 2325 served as separator and the electrolyte is 1 M non-aqueous lithium perchlorate (LiClO_4) in a mixture of ethylene carbonate (EC), diethyl carbonate (DEC) and dimethylene carbonate (DMC) in a volume ratio of EC/DEC/DMC=1:1:1. The separator and electrolyte were sandwiched by the AuNP/RGO films on the polyethylene terephthalate (PET) substrates, as shown in **Figure 10A**. The fabricated supercapacitor was flexible, as shown in **Figure 10B**, which is an optical image of the flexible multi-layered AuNP/RGO hybrid film supercapacitor using free-standing SWCNT film as current collector.

[00108] **Example 7: Cyclic voltammetry of multilayer hybrid film supercapacitors**

[00109] Cyclic voltammetry of the multilayer hybrid film supercapacitors was performed by CHI 660D instrument (CHI Instruments).

[00110] **Figure 12** is a series of graphs showing (A) cyclic voltammetry (CV) curves of the representative supercapacitors using (i) pure RGO film without SWCNT film current collector, (ii) RGO film with SWCNT film current collector, and (iii) AuNP/RGO film with SWCNT film current collector as electrodes; (B) the CVs normalized to 1; (C) the CV curves of a representative AuNP/RGO film electrode supercapacitor at different scan rates; and (D) the specific capacitance of AuNP/RGO film supercapacitors as a function of AuNP deposition time.

[00111] The CVs of the supercapacitors were found to be close to rectangular in shape within a selected range of potential, indicating an excellent capacitance behavior and that RGO-based electrode is an excellent candidate for electrochemical double-layer capacitors. The inner integrated area (current $\times$ voltage) of CV is the power density, which increases, when SWCNT films were used as current collectors. This power density will be larger, if the ESR, indicated by the slope of V/I (indicated by the dotted box in **Figure 12B**), is smaller. In order to compare slope of V/I , the CVs in **Figure 12A** were normalized to 1, as shown in **Figure 12B**. When the SWCNT films were used as current collectors, the slope of V/I were remarkably increased, indicating that the SWCNT film current collectors could effectively reduce the ESR of the supercapacitor electrodes. Besides, slope of V/I of the AuNP/RGO is larger than that of RGO film (refer to **Figure 12B**), indicating AuNP/RGO film electrode have smaller ESR in comparison with RGO film electrode. The reason may be that the addition of AuNPs will increase the conductivity of the RGO film.

[00112] **Figure 12C** shows the CV curves of a representative AuNP/RGO film electrode supercapacitor at different scan rates. Typically, the cyclic voltammetry (CV) curves of the supercapacitor device based on the RGO/AuNP hybrid films showed rectangular shape from 0 to 2.0 V over a wide range of voltage scan rates and even at a high scan rate of 1000 mV/s, indicating an excellent capacitance behavior and that the AuNP/RGO with SWCNT film current collector have very rapid current response on voltage reversal. The addition of AuNPs improves the specific capacitance of the supercapacitor, as shown in **Figure 12A**.

[00113] Also, it was suggested that the RGO/AuNP hybrid films with SWCNT film current collector have very rapid current response on voltage reversal. The specific capacitance C_{spe} was estimated from CV curves using Equation (1):

[00114]
$$C_{spe} = I/sm \quad (1)$$

[00115] where I is the corresponding current of the voltage applied (at 0.4 V), s is the scan rate, and m is the total mass of the active electrode materials. The calculated specific capacitance of the corresponding supercapacitor (120 s of AuNP deposition time) was about
5 64 F/g at a scan rate of 5 mV/s.

[00116] **Figure 13** is a typical galvanostatic charge/discharge curve at the current density of 1 A/g for the same device mentioned above. The discharge curve is nearly a straight line, indicating a good electrical double layer performance. The specific capacitance C_{spe} of supercapacitor device was calculated from constant current charge/discharge curves using
10 Equation (2):

[00117]
$$C_{spe} = \frac{I}{(dV/dt)m} \quad (2)$$

[00118] where I is the discharge current, dV/dt represents the slope of the discharge curve, and m is the total mass of the SWCNT film on both electrodes. The calculated specific capacitance of the resulting multilayer hybrid film supercapacitor is about 65 F/g, which
15 agrees well with the above result from CV testing. The calculated energy density ($W = C_{spe}V^2/2$, where V is the voltage applied) is 36 Wh/kg and the maximum power density ($P_{max} = V^2/4Rm$, where R is the internal resistance, which can be calculated using IR drop, m is the total mass of the active electrode material on both electrodes) of resulting multilayer hybrid film supercapacitor is 49 kW/kg.

[00119] As a control experiment, we also tested the supercapacitor devices made by the compact RGO films (**Figure 6**) without AuNP “spacers”. The specific capacitance, energy density and power density of supercapacitors based-on compact RGO films are 23 F/g, 13 Wh/kg and 27 kW/kg, respectively. These values reveal that the addition of the spacer, AuNPs, in the multilayer film improve effectively the performance of the RGO
25 supercapacitor electrodes. Furthermore, the specific capacitance of supercapacitor based on multilayer hybrid film is also larger than the case of reported supercapacitors using compact graphene films as electrodes, and the energy density and power density are also much larger than the case of reported graphene-based supercapacitors and the commercially available supercapacitor devices (energy density: 1-10 Wh/kg and power density: 2-10 kW/kg), which
30 are mainly based on porous activated carbon.

[00120] **Example 8: Effect of AuNP deposition time on capacitances of supercapacitors based on the RGO/AuNP hybrid films**

[00121] The specific capacitance (C_{spe}) at different AuNP deposition times was calculated and plotted, as shown in **Figure 12D**. From the results obtained, it has been surprisingly found that the specific capacitances of supercapacitors based on the RGO/AuNP hybrid films is strongly related to the AuNP deposition time. When the deposition time is less than 120 seconds, the specific capacitance of AuNP/RGO film electrode increased with an increase in deposition time. However, when the deposition time is more than 120 seconds, the specific capacitance of AuNP/RGO electrode decreased with an increase in deposition time.

[00122] AuNP layers provide a support for the reduced graphene oxide (RGO) layers and avoid the self-aggregation of RGO layers to increase the active electrochemical surface area. However, when the density of Au NPs is not large enough, Au NPs cannot support the RGO layers completely and some region of the RGO layers may aggregate. With the increase of AuNP density during initial 120 seconds, the aggregated region of the RGO layers would be separated, and finally the RGO layers could be supported completely. Therefore, the active electrochemical surface area would be increased with increase in density of AuNPs, resulting in the increase of specific capacitance with the increase of AuNP deposition time, as shown in **Figure 12D**. After the RGO layers were supported completely, if the density of Au NPs was still increased, some Au NPs would have little effect on the support for the RGO layers. However, these AuNPs would attach onto the surface of RGO layers and reduce the active electrochemical surface area, which will lead to the decrease of specific capacitance, as shown in **Figure 12D**.

[00123] **Example 9: Effect of AuNP density on specific capacitance of supercapacitors based on the RGO/AuNP hybrid films**

[00124] In order to further understand the effect of AuNP density on specific capacitance of the supercapacitors on the basis of RGO/AuNP film, we further studied the effect of scan rate on the specific capacitance of the supercapacitors with different AuNP deposition time.

[00125] **Figure 14A** is a graph showing the specific capacitance of the AuNP/RGO film supercapacitors with different deposition time at different scan rate. The specific capacitance of the AuNP/RGO film supercapacitors with different deposition time decreases continually with the increase of scan rate due to progressively less efficient infiltration of ions into the gaps between different RGO layers of the hybrid film at higher scan rates. At slower scan

rates, the diffusion of ions from the electrolyte can gain access to available gaps between different RGO layers easily and penetration of electrolytic ions into the gaps will be greatly deeper, leading to a high specific capacitance. However, when the scan rate is increased, efficient infiltration of ions into the gap between different RGO layers is progressively less, as a result, there is a reduction in capacitance.

[00126] In order to understand in depth the effect of scan rate on the specific capacitance, the curves of specific capacitance as a function of the scan rate in **Figure 14A** were normalized to 1, as shown in **Figure 14B**. AuNP layers provide a support for the reduced graphene oxide (RGO) layers and obtain the gaps between different RGO layers. Before AuNPs support the RGO layers completely, the area of gaps would be increased with an increase in the density of AuNPs, resulting in that the diffusion of ions from the electrolyte can gain access to the inner of the film easily and deeply. Therefore, at higher density of AuNPs, the specific capacitance drops less abruptly with the increase of the scan rate during the initial 120 seconds AuNP deposition time, as shown in **Figure 14B**. As discussed above, after the RGO layers were supported completely (120 seconds), if AuNPs was still deposited, these AuNPs that have little effect on the support for the RGO layers would reduce the area of the gaps and block the diffusion of ions into the inner of the film, which will make the specific capacitance drops more abruptly, as shown in **Figure 12D**.

[00127] As mentioned above, the SWCNT films have excellent electrochemical behaviors. They could be used as electrodes to explore analytical applications.

[00128] **Figure 15A** is a graph depicting the CVs of RGO film electrode using SWCNT film as current collector. At low scan rate, a pair of well-defined peaks are observed corresponding to the redox reaction of $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ and the intensities of the anodic (I_{pa}) and cathodic (I_{pc}) peaks are nearly equal, indicating that the electrochemical process on the RGO film electrode is quasi-reversible. Besides, as can be seen from **Figure 15A**, the peak-to-peak separation is increased with increase in scan rates, suggesting the quasi-reversible behavior of SWCNT film electrodes. At high scan rate, it is found that voltammograms appear increasingly distorted from the well documented macroelectrode shape. **Figure 15B** is a graph showing the CVs of AuNP/RGO film electrode using SWCNT film as current collector. Compared to RGO film, the anodic and cathodic peaks are still clear, even at a high scan rate, indicating that AuNP/RGO film achieve higher signal-to-noise (redox current peaks to background currents) ratio and sensitivity of sensors. Besides, the

redox current of the AuNP/RGO hybrid film has smaller peak separation compared to that of the RGO film. It reveals that the AuNP/RGO hybrid film electrodes would have fast electron-transfer rate in comparison with RGO film electrodes.

[00129] The I_{pa} and I_{pc} were shown in **Figure 15C** as a function of the square root of the scan rates. Before the RGO layers were supported completely (120 seconds), more region of RGO layers were supported, when more AuNPs were deposited onto the surface of RGO film, leading to achieving more active electrochemical surface area and area of gaps between different RGO layers of the film. Therefore, the diffusion of ions from the electrolyte can gain access to the inner of the film easily. Therefore, at higher density of AuNPs, the I_{pa} and I_{pc} values drop less abruptly with the increase of the scan rate during the initial 120 seconds AuNP deposition time, as shown in **Figure 15B**. However, as discussed above, after the RGO layers were supported completely (120 seconds), if more AuNPs was still deposited, these AuNPs would reduce the area of the gaps and block the diffusion of ions into the inner of the film, which will make the I_{pa} and I_{pc} drops more abruptly, as shown in **Figure 12D**.

[00130] **Example 10: Fabrication of lateral multilayer RGO/AuNP patterns**

[00131] It is noted that electrophoretic buildup only involves the process that GO sheets and NPs migrated to the conductive substrates. In principle, there are no restrictions with respect to size and topology of the substrate, so electrophoretic buildup can be used to fabricate lateral GO, RGO or RGO/AuNP patterns.

[00132] **Figure 16** is a schematic diagram of fabricating RGO/AuNP lateral pattern by electrophoretic buildup. A: a layer of photoresist is coated on a suitable substrate; B: the photoresist is patterned using photolithography; C: a multilayer GO/AuNP film is deposited on the unpatterned portions of the substrate using electrophoretic deposition; D: the multilayer GO/AuNP film is reduced to form RGO/AuNP multilayers; E: photoresist is removed.

[00133] Resist was first spin-coated on an ITO substrate at 3000 rpm (refer **Figure 16A**). Optical lithography was performed to pattern and expose the surface of ITO with resist in the form of the desired device structures (refer **Figure 16B**). After ITO electrode with desired structures was obtained, the ITO was used as positive electrode to construct multilayer GO/AuNP patterns by electrophoretic deposition using a GO aqueous solution (0.5 mg/ml) as the electrolyte (refer **Figure 16C**). The distance between the two electrodes was 0.5 cm, and the applied voltage was 6 V....

[00134] Similarly, for the deposition of AuNP layers, an aqueous AuNP solution was used as the electrolyte. The distance between the two electrodes was 0.5 cm, and the applied voltage was 6 V.

[00135] Multilayer GO/AuNP patterns on ITO glass were fabricated by repeating the above two processes. GO/AuNP patterns on ITO were then chemically reduced by hydrazine monohydrate (98%), using a similar procedure as that used for the reduction of multilayer film (refer **Figure 16D**). After chemical reduction, the ITO electrode was dipped into acetone to remove the resist on the surface ITO, and the multilayer RGO/AuNP patterns were obtained (refer **Figure 16E**).

[00136] **Figure 17** is (A) an optical microscope image; and (B) scanning electron microscopy (SEM) image of a multilayer RGO/AuNPs structure comprising two layers of RGO and two layers of AuNPs square patterns.

[00137] **Figure 18** is (A) an optical microscope image; (B) scanning electron microscopy (SEM) image of multilayer RGO/AuNP stripe patterns comprising two layers of RGO and two layers of AuNPs at low magnification; (C) SEM image of (B) at high magnification. **Figure 18C** reveals that multilayer structure could also be achieved in the RGO/AuNP patterns fabricated by electrophoretic buildup, which is similar with RGO/AuNP film. It indicates that electrophoretic buildup is an effective approach to fabricate lateral RGO/AuNP patterns with different types.

CLAIMS

1. A method of the preparation of a multilayer film comprising metal nanoparticles and a graphene-based material using electrophoretic deposition on a substrate, the method comprising
- 5 a) electrophoretically depositing a layer of graphene-based material on the substrate;
- b) electrophoretically depositing a layer of metal nanoparticles on the layer of graphene-based material;
- 10 c) optionally repeating steps (a) and (b) for one or more additional cycles; and
- d) electrophoretically depositing a layer of graphene-based material on the layer of metal nanoparticles.
- 15 2. The method according to claim 1, wherein step a) comprises
- a) preparing a suspension comprising the graphene-based material; and
- b) contacting the suspension with two electrodes to which an electrical voltage is applied, wherein the anode comprises the substrate, thereby depositing the graphene-based material on the substrate.
- 20 3. The method according to claim 1 or 2, wherein step (b) comprises
- a) preparing a suspension comprising the metal nanoparticles;
- b) contacting the suspension with two electrodes to which an electrical voltage is applied, wherein the anode comprises the substrate having the layer of graphene-based material deposited thereon, thereby depositing the metal nanoparticles on the layer of graphene-based material.
- 25 4. The method according to any one of claims 1 to 3, wherein step (c) comprises
- a) preparing a suspension comprising the graphene-based material;
- 30 b) contacting the suspension with two electrodes to which an electrical voltage is applied, wherein the anode comprises the substrate having the layers of graphene-based material and metal nanoparticles deposited

thereon, thereby depositing the graphene-based material on the layer of metal nanoparticles.

5. The method according to any one of claims 1 to 4, wherein the graphene-based material/metal nanoparticles is/are suspended in dimethylformamide.
6. The method according to any one of claims 1 to 5, wherein the graphene-based material is graphene oxide.
7. The method according to any one of claims 1 to 6, wherein the metal nanoparticles are negatively charged.
8. The method according to any one of claims 1 to 7, wherein the metal nanoparticles comprise a noble metal selected from the group consisting of gold, silver, platinum, iridium, ruthenium, rhodium and palladium.
9. The method according to claim 8, wherein the metal nanoparticles are gold nanoparticles.
10. The method according to claim 9, wherein the metal nanoparticles are citrate stabilized-gold nanoparticles.
11. The method according to claim 9 or 10, wherein the electrophoretic deposition of gold nanoparticles is carried out for a time period ranging from about 100 s to about 150 s.
12. The method according to claim 11, wherein the electrophoretic deposition of gold nanoparticles is carried out for about 120 s.
13. The method according to any one of claims 1 to 12, further comprising contacting the multilayer film comprising metal nanoparticles and a graphene-based material with a reducing agent.

14. The method according to claim 13, wherein the reducing agent is hydrazine monohydrate.
15. The method according to any one of claims 1 to 14, further comprising removing the
5 multilayer film from the substrate by immersing the substrate comprising the multilayer film in an aqueous medium.
16. The method according to any one of claims 1 to 15, wherein the substrate is patterned
10 with a photoresist.
17. The method according to claim 16, further comprising removing the photoresist on
the substrate with a suitable solvent after the multilayer film is formed.
18. A multilayer film comprising metal nanoparticles and a graphene-based material
15 obtainable by the method according to any one of claims 1 to 17.
19. A multilayer film comprising a layer of metal nanoparticles between a first layer of a
graphene-based material and a second layer of a graphene-based material.
20. The multilayer film according to claim 19, wherein the graphene-based material is
20 graphene oxide or reduced graphene oxide.
21. The multilayer film according to claim 19 or 20, wherein the metal nanoparticles
25 comprise a noble metal selected from the group consisting of gold, silver, platinum,
iridium, ruthenium, rhodium and palladium.
22. The multilayer film according to any one of claims 19 to 21, wherein the metal
nanoparticles are gold nanoparticles.

23. The multilayer film according to any one of claims 19 to 22, wherein the density of the layer of metal nanoparticles is about $150 \mu\text{m}^{-2}$ to about $450 \mu\text{m}^{-2}$
- 5 24. The multilayer film according to any one of claims 19 to 23, wherein the metal nanoparticles form a homogeneous layer between first layer and the second layer of a graphene-based material.
- 10 25. An electrode comprising a multilayer film according to any one of claims 18 to 24, wherein the graphene-based material is reduced graphene oxide.
26. The electrode according to claim 25, wherein the electrode is an electrode comprised in a supercapacitor, a sensor, a hybrid electrochemical device, a rechargeable battery, or a metal-air battery.