METHOD FOR PREPARING GRAPHENE-BASED CONDUCTING NANO-COMPOSITE FILM

Abstract: A method for preparing graphene-based conducting nano-composite film includes the steps of: providing a graphite source and oxidizing the graphite source to form graphite oxide solution, creating a dispersion of the graphite oxide solution in a liquid, thickening the graphite oxide solution to form a graphite oxide gel, providing a deposition solution and dipping it in the graphite oxide gel, providing a substrate, and applying an electric field across at least a portion of the deposition solution dipped in the graphite oxide gel for depositing at least one portion of graphene from the graphite oxide gel and the deposition solution on the substrate.

Title: METHOD FOR PREPARING GRAPHENE-BASED CONDUCTING NANO-COMPOSITE FILM

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Title: Method for Preparing Graphene-Based Conducting Nano-Composite Film

Technical Field:

Embodiments of the present invention generally relate to graphene materials, and more particularly, to methods for preparing graphene-based conducting nano-composite films.

Background Art:

In recent years, the search for new materials for use as electrodes in energy storage devices such as supercapacitors (SCs) and batteries has increased greatly mainly due to the demand for power systems with high energy and power densities. Because of environmental issues and depleting fossil fuels, interest in the development of alternative energy storage/conversion devices with high power and energy densities catering to present-day demands has increased to a greater extent. Of the various energy storage devices, supercapacitors (SCs) are considered promising candidate for applications ranging from electric vehicles to cellular phones. Moreover, supercapacitors (SCs) have received considerable attention due to its expanding arrays of application since portable electronics continue to gain in popularity. As an energy storage device, supercapacitors (SCs) bridge the gap between conventional capacitor and battery, and have been extensively studied to develop an advanced supercapacitor device. Relentless efforts have been done, especially, in searching for the novel electrode materials. Generally, there are three categories of electrode materials, i.e. carbon materials, metal oxides/hydroxides and conducting polymers.
Supercapacitors (SCs) are broadly classified into two categories, depending on the electrode materials used. The first category is electrical double-layer capacitors (EDLCs) and the second category is pseudo-capacitors, depending on the nature of charge storage mechanism. EDLCs exhibit a non-faradic reaction with accumulation of charges at the electrode-electrolyte interfaces while the pseudo capacitors show faradic redox reactions. In both of these classes of storage devices, the performance is determined by the choice of electrode materials. In operation, energy storage in EDLC results from the separation of electronic and ionic charges between electrode and electrolyte interface while a pseudo-capacitor utilizes faradaic reactions occurring within the active material of electrodes.

One of the limiting features that prevent more widespread usage of electrochemical supercapacitors has been the relatively low energy density of the materials employed in capacitive storage applications. Currently, the field is largely based on materials made of carbon and electric double layer storage processes. A significant phenomenon occurs as electroactive materials approach nanometer-scale dimensions. The charge storage of cations from faradaic processes occurring at the surface of the material, referred to as the pseudocapacitive effect, becomes increasingly important.

Carbon materials such as activated carbon and carbon nanotubes (CNTs) have been widely investigated for EDLC due to their good conductivity and excellent chemical properties. Activated, mesoporous, and carbide-derived carbons, graphene, carbon fabrics, fibers, nanotubes, onion-like carbons (OLCs), and nanohorns as well as various nanostructured polymers with high specific surface area and moderate cost have been
widely investigated for EDLC applications. In recent years, focus has been on graphene-based materials since they have shown immense theoretical and practical advantages, such as a high surface area, excellent conductivity and capacitance, and relatively low production cost.

Although existing electric double layer capacitors (EDLC’s) have high power capabilities, the energy density for electric double layer capacitors is well below that of batteries. The reason is that only the specific surface area of the carbon electrode contributes to energy storage while in the battery, the entire material, surface and bulk, contributes to the storage capacity.

Metal oxides are another grouping of materials that have been studied for use in electrochemical capacitors. The interest in using pseudocapacitor based materials for electrochemical capacitors is that the energy density associated with faradaic reactions is theoretically much higher, by at least an order of magnitude, than traditional double layer capacitance. Examples of redox metal oxides include (RUO2 and Mn02) as a promising material for pseudo-capacitor. Hydrous RUO2 had been extensively studied and its capacitance value is as high as 720 F/g in acidic electrolyte. However, the drawback of utilizing hydrous RUO2 is high production cost and toxic nature of RUO2.

Each class of electrode has identified a number of candidates as promising materials as supercapacitor electrode. However, each class has its unique advantages and disadvantages for supercapacitor application. For example, electrostatic charge storage mechanism of the EDLC electrode has very high stability during charge-discharge cycling, however, electrode of this kind may only physically store limited charges, lead to low specific capacitance.
Moreover, transition metal oxides and conducting polymers have relatively higher capacitance, challenges remain because the relatively low mechanical stability and cycle life limit their application for supercapacitors.

Although there has been extensive research involved with advancing supercapacitor technology, there remains a need for devices having higher energy densities that can still be efficiently and cost-effectively manufactured without undue environmental or safety concerns.

Moreover, there remains a need in the art for a method of fabrication of binary or ternary composites of carbon materials, conducting polymers and metal oxides as materials for supercapacitors.

**Disclosure of the Invention:**

Embodiments of the present invention aim to provide a method for preparing graphene-based conducting nano-composite film, and the method includes the steps of, providing a graphite source and oxidizing the graphite source to form graphite oxide solution, creating a dispersion of the graphite oxide solution in a liquid, thickening the graphite oxide solution to form a graphite oxide gel, providing a deposition solution and dipping it in the graphite oxide gel, providing a substrate, and, applying an electric field across at least a portion of the deposition solution dipped in the graphite oxide gel for depositing at least one portion of graphene from the graphite oxide gel and the deposition solution on the substrate.

While the invention is described herein by way of example using several embodiments and illustrative drawings, those skilled in the art will recognize that the
invention is not limited to the embodiments of drawing or drawings described, and are not intended to represent the scale of the various components. Further, some components that may form a part of the invention may not be illustrated in certain figures, for ease of illustration, and such omissions do not limit the embodiments outlined in any way. It should be understood that the drawings and detailed description thereeto are not intended to limit the invention to the particular form disclosed, but on the contrary, the invention is to cover all modification, equivalents and alternatives falling within the spirit and scope of the present invention as defined by the appended claims. The headings used herein are for organizational purposes only and are not meant to be used to limit the scope of the description or the claims. As used throughout this application, the word "may" is used in a permissive sense (i.e., meaning having the potential to), rather than the mandatory sense (i.e., meaning must). Similarly, the words "include," "including," and "includes" mean including, but not limited to. Further, the words "a" or "an" mean "at least one" and the word "plurality" means one or more, unless otherwise mentioned.

Description of Drawings and Best Mode for Carrying Out the Invention:

So that the manner in which the above recited features of the present invention can be understood in detail, a more particular description of the invention, briefly summarized above, may be had by reference to embodiments, some of which are illustrated in the appended drawings. It is to be noted, however, that the appended drawings illustrate only typical embodiments of this invention and are therefore not to be
considered limiting of its scope, for the invention may admit to other equally effective embodiments.

These and other features, benefits and advantages of the present invention will become apparent by reference to the following text figures, with like reference numbers referring to like structures across the views, wherein:

FIG. 1 is a graphical illustration of XRD spectra of (a) Glass slide with double sided tape, (b) PPy/GR 0.1M MnOₓ and (c) PPy/GR/0.5 MnOₓ, while mounting a sample during a method for preparing graphene-based conducting nano-composite film according to an embodiment of the present invention;

FIG. 2A, FIG. 2B and FIG. 2C are a graphical illustration of XPS spectra of PPy/GR/0.1 M MnOₓ at (a) Mn 2p, (b) O 1s and (c) C 1s region, according to an embodiment of the present invention;

FIG. 3A is a graphical illustration of FT-IR spectra of (a) GO and (b) PPy/GR/0.1 M MnOₓ, according to an embodiment of the present invention;

FIG. 3B is a graphical illustration of FESEM images of (a) PPy, (b) PPy/GR, (c) cross sectional view of PPy/GR, (d) PPy/GR/0.1 M MnOₓ, (e) cross sectional view of PPy/GR/0.1 M MnOₓ, (f) high magnification PPy/GR/0.1 M MnOₓ and (g) high magnification PPy/GR/0.5 M MnOₓ; (h) EDX spectrum of PPy/GR/0.1 M MnOₓ and (i) elemental mapping of PPy/GR/0.1 M MnOₓ, based on image shown in (d), according to an embodiment of the present invention;

FIG. 3C is a graphical illustration of EDX spectrum of (f) PPy/GR/0.1 M MnOₓ and (g) elemental mapping of PPy/GR/0.1 M MnOₓ, based on image shown in (c), according to an embodiment of the present invention;
FIG. 4 is a graphical illustration of CVs for PPy, PPy/GR and PPy/GR/0.1 M MnO\textsubscript{x} at a scan rate of 1 mV/s, according to an embodiment of the present invention; FIG. 5 is a graphical illustration of CVs for different concentration of MnO\textsubscript{x} at scan rate of 1 mV/s, according to an embodiment of the present invention; FIG. 6 is a graphical illustration of CVs of PPy/GR/0.1 M MnO\textsubscript{x} at different scan rates, according to an embodiment of the present invention; FIG. 7 is a graphical illustration of Galvanostatic charge/discharge curves of PPy/GR/0.1 M MnO\textsubscript{x}, PPy/GR and PPy at a current density of 1 A/g, according to an embodiment of the present invention; FIG. 8 is a graphical illustration of Nyquist plot of PPy/GR/0.1 M MnO\textsubscript{x}, PPy/GR/0.5 M MnO\textsubscript{x} and PPy/GR, according to an embodiment of the present invention; and FIG. 9 is a graphical illustration of specific capacity retention for PPy/GR/0.1 M MnO\textsubscript{x} and PPy/GR electrodes at a charge/discharge current density of 3 A/g, according to an embodiment of the present invention.

Various embodiments of the present invention aim to provide a method for preparing graphene-based conducting nano-composite film. The present method provides electrochemical doping-deposition route for simultaneous doping of polypyrrole (PPy) with pTS ions and embedding MnO\textsubscript{x} and GR. Particularly, the method includes the steps of, providing a graphite source and oxidizing the graphite source to form graphite oxide solution. In operation, graphite powder is obtained from Ashbury Graphite Mills Inc., code no. 3061. Sulphuric acid (H_2SO_4, 95-98 %), phosphoric acid
(H₂PO₄, 85 %), potassium permanganate (KMnO₄, 99.9 %), and hydrogen peroxide (H₂O₂, 30 %) is purchased from System. Hydrogen chloride (HCl, 37 %) and manganese sulphate (MnSO₄, 98-101 %) is purchased from Sigma-Aldrich and Merck. Pyrrole (99 %, Acros organic) is stored in 0°C and distilled prior to use. Sodium p-toluenesulfonate (NapTS, 98 %) is purchased from Merck. Sodium sulphate anhydrous (Na₂SO₄, 99.5 %) is purchased from BDH Chemicals.

However, the chemicals used for the preparation of the graphene-based nanocomposite film do not conform only to the chemicals used in the present invention and may include any other chemical available in the art which can be used for the preparation of the graphene-based nanocomposite film.

Preparation of GO

GO was synthesized using the simplified Hummer's method. Graphite oxide is obtained by oxidation of 3 g of graphite flakes with H₂SO₄:H₃PO₄ (360:40 ml) and 18 g of KMnO₄. The mixing process is performed using a magnetic stirrer. The mixing process is completed in about 5 minutes. However, to ensure complete oxidation of graphite, the mixture was stirred for about 3 days. During the oxidation, the colour of the mixture changed from dark purplish green to dark brown. Subsequently, H₂O₂ solution was added to stop the oxidation process, and the colour of the mixture changed to bright yellow, indicating a high oxidation level of the graphite.

In accordance with an embodiment of the present invention, the method for preparing graphene-based conducting nano-composite film further includes the steps of creating a dispersion of the graphite oxide solution in a liquid and thickening the graphite oxide solution to form a graphite oxide gel.
Preparation of graphite oxide gel

The graphite oxide formed is washed with 1 M of HCl aqueous solution and repeatedly with de-ionized water until a pH of 4-5 is achieved. The washing process is carried out using a simple decantation of the supernatant using the centrifugation technique. During the washing process with de-ionized water, the graphite oxide experienced exfoliation, which resulted in the thickening of the GO solution. Consequently, the thickening of the GO solution resulted in the formation of the GO gel. The concentration of the GO gel is about 4.38 mg/ml.

In accordance with an embodiment of the present invention, the method for preparing graphene-based conducting nano-composite film further includes the steps of providing a deposition solution and dipping it in the graphite oxide gel, providing a substrate and, applying an electric field across at least a portion of the deposition solution dipped in the graphite oxide gel for depositing at least one portion of graphene from the graphite oxide gel and the deposition solution on the substrate.

In use, the electric field results from a direct current voltage applied between the counter electrode and the working electrode for about 2 hours.

In accordance with an embodiment of the present invention, the step of creating a dispersion of the graphite oxide solution in the liquid and thickening the graphite oxide solution to form the graphite oxide gel includes exfoliating the graphite oxide in the liquid by repeatedly washing with de-ionized water.

In accordance with an embodiment of the present invention, the step of applying the electric field includes providing an electrophoresis solution including a supporting electrolyte, and forming the graphene-based conducting nanocomposite film on a
surface of the substrate by simultaneously depositing at least one portion of the deposition solution and at least one portion of graphene from the graphite oxide gel onto the surface of the substrate by an electrophoresis deposition (EPD) method in a proper electrophoresis deposition (EPD) condition. In use, the electrophoresis deposition (EPD) step is performed by a potentiostatic method. Furthermore, the potentiostatic method includes applying a potential of about +0.8 V for about two hours for depositing the deposition solution onto the surface of the substrate at room temperature.

In accordance with an embodiment of the present invention, the step of forming of the nano-composite film includes electro-chemical processing.

In accordance with an embodiment of the present invention, the deposition solution includes a conductive polymer and a manganese compound. In use, the conductive polymer is a polypyrrole, the supporting electrolyte is a sodium p-toluenesulfonate, and the manganese compound is a manganese sulphate.

In accordance with an embodiment of the present invention, the conductive polymer is used in a range of about 0.1 uM to about 10 M.

In accordance with an embodiment of the present invention, the electro-chemical processing includes installing a three electrode cell by connecting a saturated calomel electrode as a reference electrode, a graphite electrode as a counter electrode, an indium tin oxide (ITO) electrode as a working electrode and, submerging an electrode cell into the deposition solution.

In accordance with an embodiment of the present invention, the substrate is indium tin oxide coated glass.
In accordance with an embodiment of the present invention, concentration of the graphite oxide gel is about 4.38 mg/ml, and the deposition solution includes about 0.1 M of polypyrrole, about 1 mg/ml of graphite oxide gel, about 0.1 M of sodium p-toluenesulfonate, and about 0.1 mM to about 0.5 M of manganese sulphate.

In preferred embodiment of the present invention, concentration of manganese sulphate is about 0.1 M.

Preparation of PPy/GR/MnOx nanocomposite film

PPy/GR/MnOx nanocomposite films are deposited onto indium tin oxide (ITO) coated glass by potentiostatic deposition from an aqueous solution placed in a one-compartment cell. The deposition solution contains 0.1 M of pyrrole, 1 mg/ml of GO, 0.1 M of NapTS and 0.1 mM to about 0.5 M of MnSO4. Particularly, a potentiostat-galvanostat (Elchema model EQCN-502 Faraday cage) is used for the synthesis of the composite films at room temperature. The graphite electrode is used as the counter electrode and indium tin oxide (ITO) is used as the working electrode.

Moreover, a saturated calomel electrode (SCE) is used as reference electrode. The electrochemical deposition is performed at a constant potential of +0.8 V (versus SCE) for about 2 hours. For comparison, PPy film and PPy/GR film are synthesized.

Experimentation:

Characterization of Materials:

X-ray photoelectron spectroscopy (XPS) measurement, was carried out on an Axis UltraDLD (Kratos analytical Ltd). The crystalline structure of the samples were analysed using Siemens D5000 X-ray diffraction (XRD) and FT-IR spectra were recorded on a
Perkin-Elmer model 1725x. The surface morphology of samples was investigated using a field emission scanning electron microscopy (FESEM, FEI Nova Nano SEM 400).

**Electrochemical measurements:**

The electrochemical properties of the materials were measured using cyclic voltammetry (CV), galvanostatic charge-discharge and electrochemical impedance spectroscopy (EIS) on a VersaSTAT 3 electrochemical system (Princeton Applied Research). A three-electrode cell system, including composite films as the working electrode, platinum wire as a counter electrode and Ag/AgCl as the reference electrode, were employed to conduct the experiment. All the electrochemical measurements were carried out in an electrolyte of 1.0 M Na$_2$SO$_4$ solution at room temperature.

With reference to FIG. 1, illustrates the graphical illustration of XRD pattern of an empty slide with double sided tape which mounts the sample, according to an embodiment of the present invention. Particularly, the characteristic peak of polypyrrole (PPy) may be observed at 16° which corresponds to pyrrole counter ion or inter-counter ion interaction scattering, and the peak at 22.8° arises from polypyrrole (PPy) chain that is close to the inter-planar Van de Waals distance from the aromatic groups. However, at a low concentration of MnSO$_4$, the XRD pattern of the nanocomposite is similar to that of the free polypyrrole (PPy) because the oxide particles are scarcely distributed on the surface of the nanocomposite, and consequently, the XRD peaks of polypyrrole (PPy) are predominant due to transformation of the crystalline MnO$_2$ and Mn$_2$O$_3$ into amorphous phase during the deposition reaction. Generally, with an increase in MnO$_x$ concentration in the PPy/GR/MnO$_x$ nanocomposite, there are distinguishable diffraction peaks assigned to MnO$_2$ (JCPDS No. 44-0141) and Mn$_2$O$_3$ (JCPDS No. 41-1442),
which are 12.8°, 25.8°, 29.9°, 39.1° and 50.0° for MnO$_2$, and at 18.9° and 55.4° for MnO$_3$, indicating that the nanocomposite contains mixed manganese oxide.

With reference to FIG. 2A, FIG. 2B and FIG. 2C, the surface information of PPy/GR/0.1 M MnO$_x$ nanocomposites is analyzed using an XPS. The presence of manganese oxide within the matrix of PPy/GR/MnO$_x$ is evident from the Mn signals. As the contribution of manganese oxide component as a pseudo capacitor has a direct impact toward the overall electrochemical performance of the nanocomposites, precise knowledge of the oxidation state of Mn is required. Fig. 2A illustrates the Mn 2p core level spectrum which shows broad peaks of Mn 2p$_{3/2}$ and Mn2p$_{1/2}$, indicating that the nanocomposite consists of mixed Mn species at various oxidation states. Accordingly, the Mn 2p$_{3/2}$ and Mn2p$_{1/2}$ deconvoluted into four components peaks; 641.3 and 653.2 eV are attributed to Mn3+, and 642.3 and 654.2 eV are attributed to Mn4+, resulting in the formation of Mn$_2$O$_3$ and MnO$_2$, respectively. Therefore, the manganese oxide prepared is non-stoichiometric and amorphous. The areas under the associated peaks reveal the relative amounts of these components, in which MnO$_2$ (57%) is the dominant form. The existence of manganese oxide is also reflected in the O 1s core level spectrum as shown in Fig. 2B. The spectrum can be deconvoluted into four components, which are related to Mn-O-Mn oxide bond (530.4 eV), C-O or S-O bond (531.4 eV), COOH (533.7 eV) and H-O-H (532.7 eV). The C-O and COOH bonds are remnants of the oxide functional groups of the GO, and the S-O bond originates from NapTS as a dopant. The XPS C 1s core level spectrum of the nanocomposite film can be fitted into seven component peaks with binding energies of 283.0 eV, 284.2 eV, 284.6 eV, 285.2 eV, 286.2 eV, 287.3eV and 288.6eV, which are attributed to the metal
carbide, sp² hybridized carbon, sp³ hybridized carbon, C-N, C-O, C=O and COOH, respectively. The carboxyl and carboxylic groups are the remaining oxygenous groups of the GO. The presence of metal carbide component is likely due to some differential charging raised by the ejection of photoelectrons from insufficiently conductive sample surface.

With reference to FIG. 3A, the GO spectrum shows a broad and intense peak at 3355 cm⁻¹ which corresponds to OH band. The peak at 1723 cm⁻¹ and the peaks in the range of 1500-1000 cm⁻¹ are assigned to C-O functionalities namely COOH, COC/C-OH, respectively. Also, as the absorption peaks are close to one another, they overlap with each other, resulting in poorly defined peaks. The peak at 1617 cm⁻¹ is associated to the sp² character of GO. The PPy/GR/MnO₂ spectrum has a broad peak in the region of 800-400 cm⁻¹ which is attributed to the manganese oxide vibration of MnO₆ octahedron in MnO₂, which provides evidence for the oxidation of Mn²⁺ into MnO₂ in the nanocomposite during the electro deposition process. The nanocomposite spectrum illustrates the characteristic of polypyrrole. The bands at 1400 cm⁻¹ are due to aromatic ring stretching of pyrrole ring, together with band at 996 cm⁻¹ (N-H out of plane bending) and 1104 cm⁻¹ (C-N stretching) suggesting that polypyrrole (PPy) is successfully polymerized in the presence of GO and MnSO₄. Moreover, the characteristic of oxygen functionalities disappeared, indicating that the GO has been reduced to GR. From the XPS and FT-IR analyses, it may be concluded that the oxidation of Mn²⁺ and pyrrole monomers would significantly reduce GO to GR.

With reference to FIG. 3B, polypyrrole (PPy) has bubonic surface whereas PPy/GR includes a network structure of fibre-like morphology, which may be made up of
an alignment of GR and polypyrrole (PPy) through the π-electrons interaction. Fig. 3B illustrates the FESEM images of PPy, PPy/GR and PPy/GR/MnO_x. PPy has a typical granule-like surface as illustrated in Fig. 3B(a) whereas PPy/GR consists of a network structure of fibre-like morphology as illustrated in Fig. 3B(b). The cross-sectional view of PPy/GR film shows that GR and PPy were condensed into a new entity, with no clear distinction of a single component as illustrated in Fig. 3B(c).

In PPy/GR/0.1 M MnO_x, the presence of MnO_x gives rise to notable continuous, three-dimensional, porous structure rather than a dense, flat surface as it acted as spacer to prevent the stacking of graphene sheets. As may be seen in Fig. 3B(f) of PPy/GR/0.1 M MnO_x, the high magnification image illustrates the forming of large surface area of the MnO_x nodular nanograins embedded on graphene sheet, with each nodular grain diameter less than 10 nm. However, as illustrated in Fig. 3B(g), in PPy/GR/0.5 M MnO_x, many MnO_x with icicle-like morphology may be seen, which inferred that increase in concentration of MnSO_4 leads to deposition of bulk MnO_x that loses its high surface area. The presence of MnO_x gives rise to notable porous structure as it acted as spacer to prevent the stacking of graphene sheets, as illustrated in Fig. 3B(d) and Fig. 3B(e). The high magnification image of PPy/GR/0.1 M MnO_x as illustrated in Fig. 3B(f) clearly illustrates the integration of MnO_x nodular nanograins on the graphene sheet, with each nodular grain diameter less than 10 nm, hence affording a porous 3-D structure. However, in PPy/GR/0.5 M MnO_x as illustrated in Fig. 3B(g), MnO_x with icicle-like morphology is formed.

FIG. 3C is a graphical illustration of EDX spectrum of (f) PPy/GR/0.1 M MnO_x and (g) elemental mapping of PPy/GR/0.1 M MnO_x, based on image shown in (c), according
to an embodiment of the present invention. The presence of Mg is evident in the analysis of EDX analysis as illustrated in FIG. 3C, according to an embodiment of the present invention. The presence of Mn for PPy/GR/0.1 M MnO\textsubscript{x} is evident in the EDX spectrum as illustrated in Fig. 3C(h). The area of bright contrast correlates with the Mn signal map as illustrated in Fig. 3C(i). Consequently, this result coupled with the XRD and XPS results provide evidence for the presence of MnO\textsubscript{x} particles in the ternary nanocomposite.

The contrast variation of the FESEM image in Fig. 3B (d) is clearly shown in FIG. 3C (g). This result, coupled with the XRD and XPS results, provides evidence for the presence of MnO\textsubscript{x} particles in the ternary nanocomposite. Accordingly, it may be concluded that PPy/GR/MnO\textsubscript{x} provides easy electrolyte penetration and high electroactive area. In use, with a view to understand the electrochemical performance of the PPy/GR/MnO\textsubscript{x} nanocomposite electrode, cyclic voltammetry was carried out using a three-electrode one-compartment cell with 1 M of Na\textsubscript{2}SO\textsubscript{4} as the electrolyte. The potential was scanned from -0.2 to 0.7 V (versus Ag/AgCl) and the scan rate was varied from 1 to 100 mV/s. The specific capacitance values of the samples are calculated from cyclic voltammograms using the following equation:

\[ C_m = \frac{\int i}{m \cdot s} \]

where \( C_m \) is the specific capacitance in farads per gram, \( \int i \) is the integrated area of the CV curve, \( m \) is the mass of the electrode material in grams, and \( s \) is the scan rate in volts per second.

With reference to FIG. 4, CV curves recorded for PPy, PPy/GR and PPy/GR/0.1 M MnO\textsubscript{x} electrodes are illustrated, according to an embodiment of the present invention.
Generally, CV with a higher current response corresponds to higher specific capacitance. PPy/GR/MnO\textsubscript{x} electrode exhibits high output current in comparison to those of PPy and PPy/GR, indicating enhancement of charge storage in the ternary nanocomposite. The voltammogram of PPy/GR/0.1 M MnO\textsubscript{x} nanocomposite are fairly rectangular shape without obvious redox peaks, indicating the nanocomposite have ideal capacitive behaviour. The calculated specific capacitances of PPy/GR/0.1 M MnO\textsubscript{x}, PPy/GR and PPy are about 320.6 F/g, about 255.1 F/g and about 118.4 F/g. The superior charge storage of the binary nanocomposite over PPy is due to the synergistic effects between graphene and PPy. The incorporation of GR into PPy decreased the distance for electron shuttling during the electrochemical reaction as graphene enhances the electronic conductive channel, resulting in fast transportation of electrons in the PPy/GR modified electrode.

In use, the excellent electrochemical performance of PPy/GR/0.1 M MnO\textsubscript{x} compared with PPy/GR is attributed to the structural modifications of the ternary nanocomposite. This infers that the MnO\textsubscript{2} played an importance role in the growth of the film, leading to the formation of unique morphology that enhanced the performance of the ternary nanocomposite. During the growth of the PPy/GR/MnO\textsubscript{x} nanocomposite, MnO\textsubscript{x} particles coated the surfaces of individual graphene sheets, acted as spacer to prevent restacking of graphene sheets, causing the sheets to pile up to form porous, three-dimensional structure. Such morphology is most effective in facilitating the penetration of electrolyte within the matrix. Moreover, the nanoscale size of the MnO\textsubscript{x} particles within the nanocomposite greatly increased its electrochemical utilization due
to its high active surface area. Therefore, the present nanocomposite is a promising candidate for the construction of high performance supercapacitor electrode.

Two mechanisms have been proposed for charge-storage in faradaic redox MnO₂-based electrodes. The first is based on the rapid intercalation of alkali metal cations such as Na⁺ in the electrode during reduction and deintercalation upon oxidation where C⁺ = Na⁺ and H⁺ and the proposed mechanism involved a redox reaction between the III and IV oxidation state of Mn, as mentioned hereinbelow:

\[
\text{MnO}_2 + C^+ + e^- \rightarrow \text{MnOO}^+ C^+
\]

The second mechanism is adsorption of cations on the electrode surface from electrolyte, as mentioned hereinbelow:

\[
(M\text{nO}_2)_{\text{surface}} + C^+ \leftrightarrow (\text{MnOO}^+ C^+)_{\text{surface}}
\]

With reference to Fig. 5, it has been illustrated that increasing the MnSO₄ concentration attenuated the charge storage performance of the nanocomposites. The specific capacitances of the nanocomposites decreased drastically from 320.6 F/g and 207.6 F/g when 0.1 M, 0.2 M and 0.3 M of MnSO₄ were used for the preparation of the nanocomposites. The nanocomposites then show a measly increase to about 232.3 F/g with the use of 0.4 M and 0.5 M of MnSO₄ for the preparation of the nanocomposites. This is because low concentration of MnSO₄ resulted in the best performance because the nano-sized particles benefited the penetration of electrolyte giving rise to a large redox-active surface area that contributed to the material's pseudo capacitance in addition to the pseudo capacitance from PPy and EDLC from GR. On the contrary, a higher concentration of MnSO₄ led to deposition of bulk MnOₓ, as illustrated in FIG. 3B.
(e), which reduced the Μηθχ - electrolyte interfacial area, which is undesirable for fast ion kinetics and thus lowered the charge storage properties.

Additionally, the influence of scan rate is minimal on the electrochemical performance of the ternary nanocomposite, as illustrated in Fig. 6, according to an embodiment of the present invention. Even though the current density increased with scan rate, the rectangular shape of the CV curves remained the same, without depressing the CV curve, which corresponds to the rapid current response on voltage reversal at each potential end, following the ideal capacitive behaviour. The slight deviation from rectangularity of the CV curve at about 100 mV/s is attributed to the reduction of effective interaction between the ions and the electrode at the high scan rate due to lesser charge mobilization per unit time.

In use, Galvanostatic charge/discharge were carried out between -0.2 and 0.7 V versus Ag/AgCl at current density of 1 A/g in 1 M Na₂S₀₄ for PPy/GR/0.1 M MnOₓ, PPy/GR and PPy. Near-ideal EDLC behavior of the charge/discharge curves is observed by the symmetry charge and discharge slopes, where a triangle curve is observed. The slight curvatures of the slopes of the PPy and PPy/GR electrodes are indicative of the involvement of the Faradaic reaction process of the PPy, and, naturally, the curvature became more pronounced for PPy/GR/0.1 M MnOₓ, indicating extra contribution of pseudo capacitance to the system due to presence of MnOₓ in the electrode matrix.

Furthermore, electrochemical impedance spectroscopy (EIS) is performed to investigate the mechanistic aspect of PPy/GR and PPy/GR/MnOₓ electrodes. A typical Nyquist plot of an ideal capacitor shows a small semi-circle at high-medium frequency
presented in the lower left portion of the spectra followed by a vertical line along the imaginary axis in the low frequency region. As illustrated in FIG. 8, the PPy/GR electrode exhibits a slightly vertical line in the low frequency region, which reveals the involvement of Faradaic charge storage mechanism. The transition of charge storage mechanism to predominance of pseudo capacitance is seen in the PPy/GR/MnOx electrodes. The PPy/GR/0.1 M MnOx electrode illustrates a more inclined curve in the same low frequency region compared with the PPy/GR electrode, indicative of the extra involvement of Faradaic reaction process of MnOx, and the inclination of such curve is obviously seen in PPy/GR/0.5 M MnOx, suggesting the predominance of pseudo capacitance. At the high frequency region (lower left portion of the spectra), all the curves show distorted and unobvious semi-circle, attributable to good electronic conductivity of the nanocomposite films. The first intercept point of the semi-circle on the real axis represents equivalent series resistance (ESR). This value is due to the identical combination of electrolyte, internal resistance of electrode and the contacts between the electrode and current collector. On the other hand, charge transfer resistance (Ret), which relates to interfacial processes of counter ions through the electrode/electrolyte interface, can be estimated from the diameter of a semicircle. The ESR and the Ret were measured to be 31.3 Ω and 0.9 Ω for PPy/GR electrode, respectively.

In contrast, the increase in ESR and Ret for PPy/GR/0.1 M MnOx (ESR = 42.9 Ω, Rd = 1.4 Ω) and PPy/GR/0.5 M MnOx (ESR = 48.3 Ω, Ret = 1.0 Ω) has resulted from poor electronic conductivity of MnOx. The increased internal resistance of electrode with the presence of MnOx within the nanocomposites indicates the slow charge transfer
between the electrode materials and the current collector. Overall, the EIS measurement on the PPy/GR/MnO_x electrodes contributes both a fast pseudo capacitance and EDLC.

With reference to FIG. 9, the long term cycling performance of the PPy/GR and PPy/GR/0.1 M MnO_x electrodes in a potential window of -0.2 to 0.7 V (versus Ag/AgCl) were measured by the consecutive galvanostatic charge-discharge at current density of 3 A/g for 1000 cycles. As illustrated therein, the specific capacitance increased by 20% after the first cycle and the electrode thereafter reached the stability state. The initial increase of capacitance is due to incomplete used of active material, however after repetitive charge/discharge cycling, the electro active site of the nanocomposite electrodes were fully exposed to the electrolyte. Therefore, an increasing capacitance was displayed in the cyclic test. The PP/GRy electrode retained about 97% of initial capacitance after 1000 cycles, while that of the PPy/GR/MnO_x retained only about 87%. The discrepant electrochemical stability between PPy/GR and PPy/GR/MnO_x may be attributable to the manganese dissolution from the PPy/GR/MnO_x electrode, which may be related to the intercalation/de-intercalation of Na^+ within PPy/GR/MnO_x during the charge-discharge process. Such charge storage mechanism together with the continuous volume expansion/contraction of electrode, led to mechanically weak connection of MnO_x within the nanocomposite.

Therefore, as may be seen, the present invention provides a method for preparing graphene-based conducting nano-composite film based on potentiostatic polymerization developed for the preparation of ternary manganese oxide-based composite films. Particularly, the present invention provides a simple method based on
potentiostatic polymerization for the preparation of ternary manganese oxide-based composite films. Electrochemical measurements showed that the ternary composite electrode exhibited a higher electrical performance than the single or binary system. Moreover, the present ternary nanocomposite can be applied in numerous fields such as energy storage, sensing platform, solar conversion, nanoelectronics and the like. The advantage of the present invention is the ease of fabrication that requires only one step to materialize the said nanocomposite.

Furthermore, the present method of fabrication is able to deposit the said nanocomposite onto indium tin oxide coated glass. It can be used as it is or be peeled off if necessary. The ternary composites characterized using x-ray diffraction spectroscopy and x-ray photoelectron spectroscopy illustrated that the manganese oxide within the film was made up of MnO2 and Mn2O3. Electrochemical measurements showed that the ternary composite electrode exhibited a higher specific capacitance (320.6 F/g), which was attributed to the morphology of PPy/GR/MnOx ternary composite. The present method maximized the pseudo capacitive contribution from redox-active MnOx and PPy, and EDLC characteristic from graphene sheets. Long cyclic measurements showed that the specific capacitance of the ternary composite film could retain 87% of its initial value over 1000 charge/discharge cycles in the potential range of -0.2 to 0.7 V vs. SCE. Nevertheless, the dispersed MnO2 could reduce the conductivity of the ternary composite.

Various embodiments of the present invention involve the controlled synthesis of salt precursors (manganese sulphate in this case) at various concentrations. This strategy can be extended to using other kinds of precursors to prepare different kinds of
nano-sized oxides. The as-prepared manganese oxide based composite films are non-stoichiometric and responsible for the amorphous structure of MnO$_2$ and Mn$_2$O$_3$. The PPy/GR/MnO$_x$ ternary nanocomposite film, particularly with the lowest MnO$_x$ concentration, has the highest specific capacitance due to the contribution of the redox process of co-deposited MnO$_x$ particles. The PPy/GR/MnO$_x$ ternary nanocomposite has promising electrochemical stability with a long life span over 1000 cycles.

It is to be understood that the above description is intended to be illustrative, and not restrictive. Many other embodiments will be apparent to those of skill in the art upon reading and understanding the above description. On the contrary the intention is to cover all modifications, alternative constructions, equivalents and uses falling within the spirit and scope of the invention should, therefore, be determined with reference to the appended claims, along with the full scope of equivalents to which such claims are entitled.
CLAIMS:

1. A method for preparing graphene-based conducting nano-composite film, said method comprising the steps of:

   providing a graphite source and oxidizing said graphite source to form graphite oxide solution;
   creating a dispersion of said graphite oxide solution in a liquid;
   thickening said graphite oxide solution to form a graphite oxide gel;
   providing a deposition solution and dipping it in said graphite oxide gel;
   providing a substrate; and

   applying an electric field across at least a portion of said deposition solution dipped in said graphite oxide gel for depositing at least one portion of graphene from said graphite oxide gel and said deposition solution on said substrate.

2. The method of claim 1, wherein said step of creating a dispersion of said graphite oxide solution in said liquid and thickening said graphite oxide solution to form said graphite oxide gel comprises exfoliating said graphite oxide in said liquid by repeatedly washing with de-ionized water.

3. The method of claim 1, wherein said step of applying said electric field comprises providing an electrophoresis solution comprising a supporting electrolyte; and forming said graphene-based conducting nanocomposite film on a surface of said substrate by simultaneously depositing said at least one portion of said deposition solution and said
at least one portion of graphene from said graphite oxide gel onto said surface of said substrate by an electrophoresis deposition (EPD) method in a proper electrophoresis deposition (EPD) condition.

4. The method of claim 3, wherein the step of forming of said nano-composite film comprises electro-chemical processing.

5. The method of claim 1, wherein said deposition solution comprises a conductive polymer and a manganese compound.

6. The method of claim 4, wherein said electro-chemical processing comprises:
   installing a three electrode cell by connecting a saturated calomel electrode as a reference electrode, a graphite electrode as a counter electrode, an indium tin oxide (ITO) electrode as a working electrode; and,
   submerging an electrode cell into said deposition solution.

7. The method according to claim 3, wherein said electrophoresis deposition (EPD) step is performed by a potentiostatic method.

8. The method according to claim 7, wherein said potentiostatic method comprises applying a potential of about +0.8 V for about two hours for depositing said deposition solution onto said surface of said substrate at room temperature.
9. The method of claim 5, wherein said conductive polymer is a polypyrrole.

10. The method according to claim 1, wherein said supporting electrolyte is a sodium p-toluenesulfonate.

11. The method according to claim 1, wherein said manganese compound is a manganese sulphate.

12. The method of claim 1, wherein said substrate is indium tin oxide coated glass.

13. The method of claim 1, wherein concentration of said graphite oxide gel is about 4.38 mg/ml.

14. The method of claim 1, wherein said deposition solution comprises about 0.1 M of polypyrrole, about 1 mg/ml of graphite oxide gel, about 0.1 M of sodium p-toluenesulfonate, and about 0.1 mM to about 0.5 M of manganese sulphate.

15. The method of claim 1, wherein said electric field results from a direct current voltage applied between said counter electrode and said working electrode for about 2 hours.

16. The method of claim 5, wherein said conductive polymer is used in a range of about 0.1 uM to about 10 M.
17. The method of claim 1, wherein concentration of manganese sulphate in said deposition solution is about 0.1 M.
(a) Glass slide - double sided tape

(c) PPy/GR/0.5 M MnOx

(b) PPy/GR/0.1 M MnOx

Δ MnO₂
δ Mn₃O₄

FIG. 1
FIG. 3A
A. CLASSIFICATION OF SUBJECT MATTER
C01B 31/02(2006.01)i, C01B 31/04(2006.01)i, H01G 11/36(2013.01)i, H01M 4/583(2010.01)i

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

B. FIELDS SEARCHED
Minimum documentation searched (classification system followed by classification symbols)
C01B 31/02; C01B 31/00; H01B 1/04; C01B 31/04; C25D 13/00; H01G 11/36; H01M 4/583

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean utility models and applications for utility models
Japanese utility models and applications for utility models
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal) & Keywords : graphene, nano, film, graphite, graphite oxide, gel, substrate, electric field, electrophoresis deposition

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
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<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
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<td>A</td>
<td>US 2013-0156678 AI (BANERJEE, SARBAJIT et al.) 20 June 2013</td>
<td>1-17</td>
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<td></td>
<td>See abst ract; paragraphs [0031], [0035], [0039H0043], [0050], [0051]; claim s 1, 2, 5, 12, 13.</td>
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<td>A</td>
<td>US 2011-0227000 AI (RUOFF, RODNEY S. et al.) 22 Sept ember 2011</td>
<td>1-17</td>
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<td></td>
<td>See abst ract; paragraphs [0032], [0035], [0039], [0040]; claims 1, 4-12.</td>
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<td>A</td>
<td>CN 103115238 A (UNIV. ZHEJIANG OCEAN) 22 May 2013</td>
<td>1-17</td>
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<td></td>
<td>See abst ract; paragraphs [0003], [0005]- [0007]; claims 1-5.</td>
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<td>A</td>
<td>CHOI, HYUN-JUNG et al., Graphene for energy conversion and storage in fuel c ell s and super capacitors, Nano Energy, 2012, Vol. 1, No. 4, Pages 535-551</td>
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<td>See abst ract; pages 535-536.</td>
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Further documents are listed in the continuation of Box C.  See patent family annex.

* Special categories of cited documents:
  * "A" document defining the general state of the art which is not considered to be of particular relevance
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  * "O" document referring to an oral disclosure, use, exhibition or other means
  * "P" document published prior to the international filing date but later than the priority date claimed

"Y" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

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<td></td>
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