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(54) Title: METHOD FOR PREPARING CATALYSST-ASSISTED POLYPYRROLE NANOPARTICLES DECORATED GRAPHENE FILM FOR HIGH-PERFORMANCE SUPERCAPACITOR

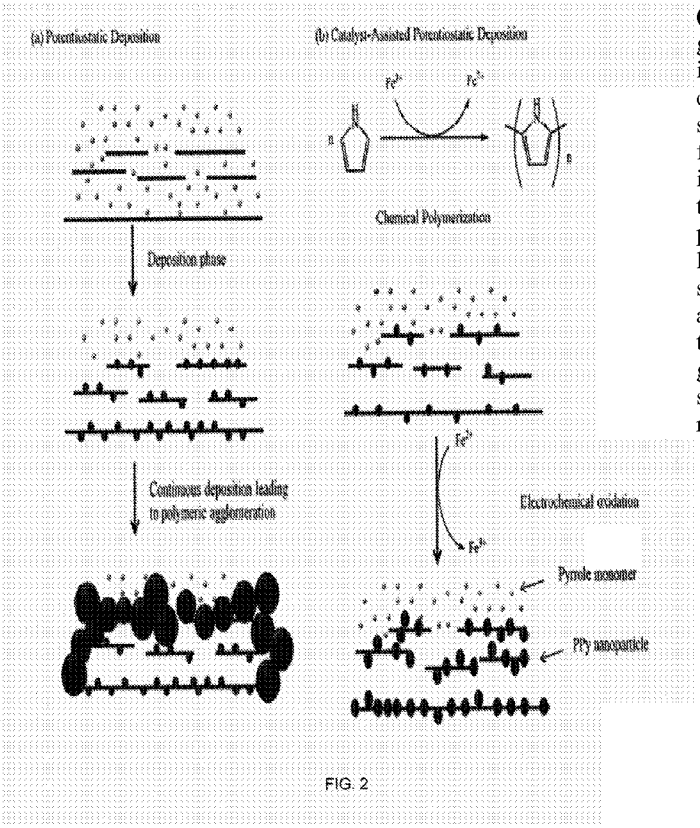

FIG. 2

(57) Abstract: A method for preparing polypyrrole and graphene nanocomposite films includes the steps of: washing the graphite oxide solution for thickening the 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, introducing at least one reagent into an one-compartment cell, providing a deposition solution and dipping it in the graphite oxide gel, stirring the deposition solution for a particular time period, reacting the at least one reagent to form polypyrrole within the deposition solution, 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 to form polypyrrole and graphene nanocomposite films.

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Title: Method for Preparing Catalyst-Assisted Polypyrrole Nanoparticles Decorated Graphene Film for High-Performance Supercapacitor

Technical Field:

Embodiments of the present invention generally relate to graphene materials, and more particularly, to methods for preparing catalyst-assisted polypyrrole nanoparticles decorated graphene film and suitable for use in electrochemical devices such as supercapacitors.

Background Art:

Graphene is a two-dimensional planar allotrope of carbon in which carbon atoms are formed in a honeycomb lattice structure, and has a high charge mobility of about 20,000-50,000 cm/Vs and a very high theoretical specific surface area of 2,630 m^2/g. In recent years, research into the application of graphene to electrochemical devices such as supercapacitors (SCs) having very high capacitance or electric double-layer capacitors is ongoing in full swing. Moreover, graphene is light, highly flexible and mechanically strong (resisting tearing by AFM tips), and the material's dense atomic structure makes it impermeable to gases. Furthermore, the combination of high electrical conductivity, good mechanical properties, high surface area, and low manufacturing cost make graphene an ideal candidate material for electrochemical applications.

Graphene oxide (GO), obtained through treating graphite with a strong oxidizer, whose basal planes and edges are abundant with various oxygen-containing group, has

also attracted great interest recently. The oxygen-containing groups such as epoxy, hydroxyl, ether and carbonyl promote good solubility in polar solvent and render versatility for the construction of GO-based hybrid nanocomposites, hence, expanding their potential applications. Recently, methods of utilizing graphene resulting from such oxidation-reduction as the electrodes of supercapacitors (or ultracapacitors) have been devised, by which the fabrication of supercapacitors having a specific capacitance of about 80 F/g or more has been reported. (R. S. Ruoff, Nano Left., 2008, 8 (10), pp 3498-3502).

Moreover in the 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.

Conducting polymers such as polypyrrole (PPy) have been studied in great detail over the years because of their unique metal-like electrical properties as well as highly desirable polymeric characteristic such as flexibility, low density, and ease of structural modification, lead to many new possibilities for device fabrication. In the current research and development activities interest of companies' world over has developed in using PPy as electrode material for supercapacitors (SCs) owing to the ease of preparation, stability in ambient conditions and relatively high conductivity. Moreover, polypyrrole is considered as one of the most promising electrode materials. Recently, there have been attempts to hybridize PPy/carbon nanocomposite materials as supercapacitor electrodes, in which high capacitance and good stability have been achieved due to the synergistic effect between them. Efforts have been done to incorporate GR and its derivatives into PPy-based nanocomposite materials to harness its unique properties.

In addition, a variation of electrode synthesis methods has been employed to create PPy/GR hetero structures. Particularly, one-pot electrochemical copolymerization onto a substrate may be one of the best ways to fabricate electrode materials. However, electrochemical copolymerization with GR suffer from polymeric aggregation where the polymer often blocks electrolyte channels on the outer surface forming a dense polymer layer that completely envelopes GR sheets. This leads to high electrode resistance due to poor interconnection between conductivity structures. Due to the dense layer of polymer on the surface of the composite film, penetration of electrolyte into the bulk of the composite material is very difficult. When a relatively thicker film is used for electrode fabrication, the charge transfer kinetics is limited due to poor electronic

conductivity and difficulty in the penetration of electrolyte into the bulk of the composite. These have been considered as the main cause of reduction of practical specific capacitance value of PPy/GR nanocomposite because only the surface of the film takes part in the charge storage process.

In a recent study, Davies *et al.* synthesized a high performance supercapacitor using pulse electropolymerization of PPy onto a pre-synthesized GR film, and demonstrated an improved uniformity of PPy coating on GR. Although a conformal coating of PPy on the pre-synthesized GR film is achieved, however, the pre-synthesized GR sheets have a high tendency to restack themselves during the preparation of graphene, leaving behind inter-graphene pore sizes that are not sufficient for accessibility to the electrolyte and the formation of EDL charges. Hence, coating PPy onto pre-synthesized GR film will also reduce the practical specific value of GR.

Consequently, to fully harness the pseudocapacitance of PPy and EDLC of GR in PPy/GR nanocomposite, the pore accessibility of GR as well as the particle size of PPy coated on GR sheets is a critically important issue and substantial improvements have to be made for its commercialization. The challenges will be control of particle size of PPy grows on individual GR sheets during the electrochemical deposition and at the same time prevent restacking of GR sheets during the process. It has been reported that particle size and morphology of PPy film may be controlled and altered by combining the chemical and electrochemical polymerization through addition of a catalyst to the electrochemical deposition setup.

Thus, a need exists in the art to develop further nano-size PPy particles which are polymerized by catalyst coated homogeneously onto individual GR sheets and such

nano-size PPy particles are suitable to be used for supercapacitors and which overcome at least some of the problems referred to above. Moreover, there remains a need in the art for PPy nanoparticles which will act as spacer to prevent the restacking of individual GR sheets.

Disclosure of the Invention:

Embodiments of the present invention aim to provide a method for preparing polypyrrole and graphene nanocomposite films, and the method includes the steps of: providing a graphite source and oxidizing the graphite source to form graphite oxide solution, washing the graphite oxide solution for thickening the 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, introducing at least one reagent into an one-compartment cell, providing a deposition solution and dipping it in the graphite oxide gel, stirring the deposition solution for a particular time period, reacting the at least one reagent to form polypyrrole within the deposition solution, 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 to form polypyrrole and graphene nanocomposite films.

In yet another embodiment of the present invention, the invention aim to provide a catalyst-assisted polypyrrole nanoparticles decorated on graphene film. Particularly, the nanocomposite film prepared by a method includes the steps of providing a graphite source and oxidizing the graphite source to form graphite oxide solution, washing the

graphite oxide solution for thickening the 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, introducing at least one reagent into an one-compartment cell, providing a deposition solution and dipping it in the graphite oxide gel, stirring the deposition solution for a particular time period, reacting the at least one reagent to form polypyrrole within the deposition solution, 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 to form polypyrrole and graphene nanocomposite films.

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 thereto 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 an illustration of FESEM images of the surface of (a) C-PPy, (b) PPy, (c) 1.0 mM Fe C-PPy/GR, (d) Cross sectional view of 1.0 mM Fe C-PPy/GR, (e) High magnification of (d), and (f) HRTEM image of 1.0 mM Fe C-PPy/GR, according to an embodiment of the present invention;

FIG.2A is a schematic diagram illustrating a potentiostatic electropolymerization (continuous deposition) process and FIG.2B is a schematic diagram illustrating a whole

catalyst-assisted electropolymerization process, according to an embodiment of the present invention;

FIG.3 is a graphical illustration of FESEM images of the (a) top view of PPy/GR, (b) cross sectional view of PPy/GR, (c) top view of 0.25 mM Fe C-PPy/GR, (d) cross sectional view of 0.25 mM Fe C-PPy/GR, (e) top view of 0.5 mM Fe C-PPy/GR and (f) cross sectional view of 0.5 mM Fe C-PPy/GR, according to an embodiment of the present invention;

FIG.4A is a graphical illustration of wide scans of GO, C-PPy, and C-PPy/GR nanocomposite film, and FIG.4B is a graphical illustration of de-convoluted XPS spectra of GO, C-PPy, and C-PPy/GR nanocomposite film, according to an embodiment of the present invention;

FIG.5 is a graphical illustration of XRD pattern of GO, PPy, PPy/GR and C-PPy/GR, according to an embodiment of the present invention;

FIG.6 is a graphical illustration of Raman spectra of GO, C-PPy and C- PPy/GR, according to an embodiment of the present invention;

FIG.7 is a graphical illustration of FT-IR spectra of GO and C-PPy/GR according to an embodiment of the present invention;

FIG.8A is a graphical illustration of CVs for PPy, C-PPy, PPy/GR, 0.25 mM Fe C-PPy/GR, 0.5 mM Fe C-PPy/GR and 1.0 mM Fe C-PPy/GR at a scan rate of 2 mV/s, and FIG.8B CVs of 1.0 mM Fe C-PPy/GR nanocomposite at various scan rate (100-2 mV/s), according to an embodiment of the present invention;

FIG.9 is a graphical illustration of Galvanostatic charge/discharge curves for the 1.0 mM Fe C-PPy/GR, PPy/GR, C-PPy and PPy electrodes for comparison at a current density of 1 A/g, according to an embodiment of the present invention;

FIG.10 Nyquist plot of C-PPy/GR and PPy/GR, according to an embodiment of the present invention; and

FIG.11 Specific capacity retention for 1.0 mM C-PPy/GR and PPy/GR electrodes at charge/discharge current density of 1 A/g, according to an embodiment of the present invention.

Various embodiments of the present invention aim to provide a method to control the particle size of polypyrrole coated on individual graphene using a catalyst-assisted electrochemical deposition technique for supercapacitor electrode. The present method provides synthesis of catalyst-assisted polypyrrole/graphene (C-PPy/GR) nanocomposite potentiostatically with the addition of $FeCl_3$ catalyst to the deposition setup with differing catalyst amount used in an effort to control the size of pyrrole on graphene for homogenous coating and avoid polymeric aggregation aimed for synergistic capacitive ability.

Particularly, the main objective of present invention is to prepare an optimized homogenous C-PPy/GR nanocomposite film that provides high performance to be utilized for supercapacitor application. It should be noted, that in the present nanocomposite film, nano-size PPy disperse homogeneously on the GR, preventing restacking of the GR layer that offers a unique three-dimensional open structure which facilitates diffusion of electrolyte, resulting in impressive electrochemical properties.

Particularly, the method includes the steps of, applying the electric field includes providing an electrophoresis solution includes a supporting electrolyte, and forming the graphene-based conducting nanocomposite film on a surface of the substrate. Particularly, the nanocomposite film is formed on the surface of the substrate by simultaneously depositing the at least one portion of the deposition solution and the 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 one embodiment of the present invention, the step of forming of the nano-composite film includes electro-chemical processing and the time period is about 30 minutes to allow polypyrrole to form in the deposition solution.

In one embodiment of the present invention, the deposition solution includes a conductive polymer.

In one 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 one embodiment of the present invention, the electrophoresis deposition (EPD) step is performed by a potentiostatic method.

In one embodiment of the present invention, 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 one embodiment of the present invention, the reagent includes metal catalyst and the metal catalyst is Iron (III) chloride.

In one embodiment of the present invention, the conductive polymer is a polypyrrole and a supporting electrolyte is a sodium p-toluenesulfonate.

In one embodiment of the present invention, the substrate has an active surface and the active surface is conductive.

In one embodiment of the present invention, the active surface is selected from graphite, Indium-Tin-Oxide (ITO), glass, which may or may not be coated with a metal.

In one embodiment of the present invention, the active surface is selected from an electrode and a metal (or alloy) coated glass.

In one embodiment of the present invention, the liquid is an acid solution and the acid solution is hydrochloric acid.

In one embodiment of the present invention, concentration of the graphite oxide gel is about 4.38 mg/ml.

In one embodiment of the present invention, the deposition solution includes at least one of a polypyrrole of about 0.1 M, about 1 mg/ml of graphite oxide gel, about 0.1 M of sodium p-toluenesulfonate, and about 0.25-1.0 mM of Iron (III) chloride.

In one embodiment of the present invention, the electric field results from a direct current voltage applied between the counter electrode and the working electrode for about 2 hours.

In one embodiment of the present invention, the catalyst-assisted polypyrrole/graphene nanocomposite film is prepared by a method which includes the steps of providing a graphite source and oxidizing the graphite source to form graphite

oxide solution, washing the graphite oxide solution for thickening the 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, introducing at least one reagent into an one-compartment cell, providing a deposition solution and dipping it in the graphite oxide gel, stirring the deposition solution for a particular time period, reacting the at least one reagent to form polypyrrole within the deposition solution, 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 to form polypyrrole and graphene nanocomposite films.

Morphology of polypyrrole/graphene nanocomposite resulted from such techniques maximize the pseudocapacitive contribution of redox-active polypyrrole and electrical double layer capacitance (EDLC) contribution from individual graphene sheets.

Specific capacitance as high as 797.6 F/g was obtained when 1.0 mM of $FeCl_3$ catalyst was added into the deposition solution, which was approximately four times higher than that of polypyrrole film and 2.6 times higher than that of polypyrrole/graphene nanocomposite in the absence of catalyst. This increase was attributed to the controlled particle size of polypyrrole growth on individual graphene sheets that prevented the overlapping of graphene sheets. This gives rise to a highly open structure which provided an easier access of electrolyte into the nanocomposite film.

FIG.1 is an illustration of FESEM images of the surface of (a) C-PPy, (b) PPy, (c) 1.0 mM Fe C-PPy/GR, (d) Cross sectional view of 1.0 mM Fe C-PPy/GR, (e) High magnification of (d), and (f) HRTEM image of 1.0 mM Fe C-PPy/GR, according to an embodiment of the present invention. Particularly, in the presence of Fe^{3+} ion as a catalyst in the deposition solution, the C-PPy film shows densely generated dendrite structure 105 of the present invention. In contrast, the PPy film grown in the absence of $FeCl_3$ by the same process has typical cauliflower morphology 110. The PPy rods are possibly formed through micelle guided growth process, a phenomenon that has been observed with amphiphilic dopants, such as β-napthalenesulfonic acid, pyrenesulfonic acid and p-toluenesulfonic acid.

Consequently, the own surfactant characteristic of pTS ions form micelles in the electrolyte solution where the hydrophobic pyrrole monomer is dissolved in micelles cluster. The addition of oxidizing catalyst will polymerise the pyrrole monomer around the pTS micelle cluster that fuction as "template like" in forming the C-PPy rod. During the electrochemical deposition, those rods formed in the deposition solution electropolymerise onto the ITO glass. However, when GO is added, the chemical polymers nano-PPy adheres onto the GO before the growth into rod-like PPy through micelles. After that, during electropolymerisation, the nano-PPy/GO sheets adheres to one another randomly and at the same time GO would be reduced to GR to form the C-PPy/GR composite.

Fig.1 illustrates top view of the catalyst-assisted electrochemical deposition of C-PPy/GR nanocomposite film with the addition of 1.0 mM $FeCl_3$ and the image reveals an extended porous and open structure 115 of the C-PPy/GR film. A cross sectional

view 120 of the nanocomposite film depicts a highly porous, 3 D structure formed from the random overlapping of GR sheets. A magnified image of a single GR sheet shows that the PPy nano-particles 125 assembly homogeneously on the GR sheet. Particularly, PPy nanoparticles assemblies on GR sheet separate the neighboring GR sheets, accountable in forming sheets that bind to one another, resulting in a highly porous structure. Moreover, the porous and 3D structure is most effective in facilitating penetration of electrolyte and increase the pseudocapacitive contribution of nano-PPy. To confirm the morphology seen in the FESEM image of C-PPy/GR nanocomposite, HRTEM was used to visualize the structure of 1.0 mM Fe C-PPy/GR. Fig.1F illustrates black aggregates for PPy 130 has been homogeneously coated on GR sheets. The particle sizes of PPy are well controlled with diameter between 5-10 nm.

Fig. 2A illustrates the deposition process in the absence of a catalyst. The pyrrole monomers within the vicinity of the electrodeposition area are electropolymerized and precipitated as PPy particles on the ITO as well as the adjacent GO sheets. When the pyrrole monomer concentration within the vicinity of the electrodeposition area is restored by diffusion from the bulk solution, the electrodeposition process continue to take place on the surface of the film made up of the PPy particles instead. This is because the formation of a layer of film acts as a barrier that prevents the diffusion of additional pyrrole monomers into the intercalating spaces between the GR sheets, leading to the thick coating of PPy on the GR sheets. Furthermore, polymeric aggregation worsens by the likelihood for electropolymerization to continue on any given polymer chain rather than nucleation of a new chain, which tend to enlarge present polymer particle. Simultaneously, the free electrons released from the formation

of PPy would reduce GO to GR during the electrochemical deposition process. This result in large and continuous PPy particles coated on the GR surface but with little penetration into the inner layer of GR sheets, leading to the formation of dense, flat surface and blocking the electrolyte channel. Such morphology reduces the contribution of pseudo capacitance from PPy and EDLC from GR since only surface of the film take part in the charge storage process.

FIG.2B is a schematic diagram illustrating a whole catalyst-assisted electropolymerization process, according to an embodiment of the present invention. To conduct a catalyst-assisted deposition, a low concentration of Fe^{3+} is added into the solution. Fe^{3+}-catalyzed polymerization may also occur in addition to electropolymerization. The Fe^{3+} catalyst oxidize the pyrrole monomers to form PPy nanoparticles that decorate the individual GO sheets, simultaneously reducing Fe^{3+} to Fe^{2+}. The subsequent electrodeposition process will unite the nano-PPy/GO sheets to one another and reduce the GO to GR, forming the scaffold of the C-PPy/GR composite. The addition of the catalyst results in uniform deposition of nano-PPy throughout the graphene film. Subsequently, maximize the expose surface area of PPy and prevent the GR sheets restack by interrupting the forming of π-π interaction between neighboring GR sheets. Fe^{3+} is regenerated simultaneously with the electrochemical oxidation of PPy nanoparticles and can be used again to synthesize PPy nanoparticles.

Particularly, to quantify the effect of differing $FeCl_3$ amount on the morphology of PPy/GR nanocomposite, FESEM is used to characterize C-PPy/GR nanocomposite films prepared using various catalyst concentrations added into the deposition solution.

Regardless of the catalyst concentration, the C-PPy/GR nanocomposites have a 3-D porous structure. However, the formation of nano-size PPy particles is dependent upon the amount of the catalyst added. In general, as the amount of the catalyst is increased, the extent of nanostructuring of PPy on GR surface also increased. Fig. 3A depicts the top view of PPy/GR prepared in the absence of $FeCl_3$, which has a dense, flat surface, which is made up of an alignment of GR and PPy through the π-electrons interaction. Fig. 3B depicts the cross sectional view of the film, which consist of few layers made up of GR and PPy, agglomerated densely together. With the addition of 0.25 mM of $FeCl_3$ into the deposition solution, a waxy but porous surface is yielded as illustrated in Fig.3C, and its cross sectional view shows reduced polymeric agglomeration as illustrated in Fig.3D, much unlike that is prepared without the catalyst. As the concentration of $FeCl_3$ is further increased to 0.5 mM, the deposition of the polymer is retarded, as illustrated by the scarcity of polymeric aggregation as illustrated in Fig.3E. Fig.3F illustrates a cross sectional view resembling that of the film grown electrochemically with 1.0 mM $FeCl_3$.

The FESEM images of C-PPy/GR shows that the morphology can be controlled with combined polymerization processes (chemical polymerization and electropolymerization). Polymeric aggregation can be efficiently suppressed, forming nano-PPy particles homogeneously on GR when 1.0 mM of $FeCl_3$ catalyst is added into the deposition solution. The changes of morphology are mainly due to the concentration of catalyst added into the deposition solution. Without the presence of catalyst in the deposition solution, the resulted morphology comprises dense layer with flat surface morphology. However, when 0.25 mM $FeCl_3$ is added, the polymeric agglomeration is

reduced and the surface becomes more porous. When the concentration of catalyst increases (0.5 mM $FeCl_3$), polymeric agglomeration is minimal. Nanostructured PPy is formed on the GR sheets when $FeCl_3$ is increased to 1.0 mM. Polymeric aggregation is completely inhibited, resulting in the decoration of nano-PPy on the GR surface that act as spacer where restacking of GR is successfully prevented.

FIG.4A is a graphical illustration of wide scans of GO, C-PPy, and C-PPy/GR nanocomposite film, and FIG. 4B is a graphical illustration of de-convoluted XPS spectra of GO, C-PPy, and C-PPy/GR nanocomposite film, according to an embodiment of the present invention. X-ray photoelectron spectroscopy (XPS) is used to confirm the functional groups of the prepared nanocomposite. Fig. 4A illustrate the wide scan and Fig. 4B illustrate de-convoluted C_{1s} XPS spectra of GO, C-PPy and C-PPy/GR.

The peak at 399.6 eV in the full XPS spectrum of C-PPy/GR indicates the presence of nitrogen from the PPy on the GR. The C_{1s} core level spectrum of the GO film can fit into five component peaks with binding energies at about 284.3, 285.3, 286.6, 287.0 and 288.6 eV, attributed to the sp^2 hybridized carbon, sp^3 hybridized carbon, C-O, C=O and COOH species, respectively. The XPS spectrum of the pure PPy film demonstrated four component peaks, which are observed at 283.9 eV, 284.4 eV, 284.9 eV and 286.3 eV, suggesting the presence of sp^2 hybridized carbon, sp^3 hybridized carbon, C-N groups and the C-S group from NapTS as a dopant. The XPS C_{1S} core level spectrum of the PPy/GR nanocomposite film can fit into six component peaks with binding energies of 283.8 eV, 284.5 eV, 285.0 eV, 286.2 eV, 287.7eV and 289.0 eV, which are attributed to sp^2 hybridized carbon, sp^3 hybridized carbon, C-N, C-O, C=O and COOH. The oxygenated carbons are detected in the XPS spectrum of C-PPy/GR, but the

intensities of these peaks have far diminished from those in GO. The results indicate the deoxygenation of graphene oxide is during the electrodeposition process.

The obtained nanocomposites were further confirmed by XRD, as illustrated in Fig. 5. The XRD pattern of the GO revealed an intense, sharp peak centered at $2\theta = 9.9^{\circ}$, corresponding to an interlayer spacing (d-spacing) of 0.89 nm. The value of interplanar spacing depends the oxygen functionality on the surface of GO. For PPy and C-PPy, a broad asymmetric peak is observed from $2\theta = 11^{\circ}$ to 30°, indicating that PPy is amorphous. The broad peak comprises of two peaks at $2\theta = 16^{\circ}$ and 22.8°. The high angle peak arises from PPy chain that is close to the inter-planar Van de Waals distance for aromatic groups and the peak at 16° corresponds to pyrrole counter ion, or intercounter ion interactions scattering. In the case of the PPy/GR and C-PPy/GR nancomposites, it presents crystalline peaks similar to that of PPy film, which ascribed to the diffraction peak of PPy. The absence of typical GO peaks for all nanocomposites indicated that the GO had been reduced to GR during the electrodeposition process. From the XRD pattern of C-PPy/GR and C-PPy, there is no defined diffraction peak and the peaks are widened. This may due to amorphous nano-PPy homogeneously coated on GR sheets, rather than more orderly coated polymeric agglomeration in PPy/GR nanocomposite and for C-PPy, the rod like structure may be less orderly compared with the typical cauliflower structure of PPy.

Moreover, the Raman spectra obtained for GO, C-PPy and C-PPy/GR are shown in Fig. 6. In the spectrum obtained for catalyst-assisted PPy, band located at 935, 981, and 1052 cm^{-1} can be assigned to C-H out-of-plane deformation, ring deformation and C-H in plane deformation, respectively. The band at 1380 and 1577 cm^{-1} are attributed

to ring stretching and C=C backbone stretching of PPy. These characteristic bands for PPy are also observed in the Raman spectra obtained from C-PPy/GR. Nevertheless, it also exhibits the characteristic D band (1357 cm^{-1}) and G band (1582 cm^{-1}) of GO in the nanocomposite film. The G band corresponds to the vibration of sp^2 hybridized carbon while the D band indicates the defect or edge plane in the structure. Therefore, the D/G intensity ratio (I_D:I_G) expresses the atomic ratio of sp^2/sp^3 carbons, to measure the extent of disordered graphite. The calculated I_D:I_G ratio for GO is 0.89, which indicates extensive oxidation of GO in the process of chemical oxidation of graphite, leading to a reduction in the size of the in-plane sp^2 domains. Compare to GO, the I_D: I_G ratio (0.76) of C-PPy/GR significantly decrease after reduction, indicating the conversion of GO into GR. The relatively large sp^2 domains of nanocomposite film indicating increase π-electron conjugation within the sp^2 domain. As a result, the spectrum of nanocomposite shows a red-shift in the G band (1582 cm^{-1}) as compared to GO (1600 cm^{-1}), another evidence that the reduction of GO indeed takes place. To further characterize the C-PPy/GR reduction process, Fourier-transform (FT-IR) spectroscopy is performed. The spectra of GO in Fig. 7 illustrates a broad and intense peak at 3355 cm^{-1} corresponding to OH peak. The peak in the 1723 cm^{-1} and peak in the range of 1400-1000 cm^{-1} correspond to C-O functionalities; COOH, COC/C-OH respectively, since the absorption range are close to one another, peak at 1400-1000 cm^{-1} overlap each other forming a broad peak. These absorption bands are typical of GO. From the spectra of catalyst-assisted PPy/GR, the absorption bands related to oxygen containing groups on GO diminished, proving that GO entrapped in the PPy matrix had been effectively reduced. Moreover, the peaks at 1514, 1430, 1119 and 1003 cm^{-1} correspond to N-H bend,

aromatic ring stretching, C-N stretching and N-H out-of-plane bending of PPy, showing the presence of PPy in the nanocomposite film.

Furthermore, CV is well known as an effective tool to investigate the capacitive behavior of a material. If the material is an ideal capacitor, it will exhibit several characteristics; high current, rectangular form of the voltammogram and symmetry in anodic and cathodic directions. In this study, the cyclic voltammetry was carried out using a three-electrode one-compartment cell with 1 M of Na_2SO_4 as the electrolyte. The potential was scanned from -0.2 to 0.8 V (versus Ag/AgCl) and the scan rate is varied from 2 to 100 mV/s.

CV curve recorded for PPy, PPy/GR and C-PPy/GR electrode is illustrated in Fig. 8A. Generally, voltammograms with a higher current response correspond to higher specific capacitance. All C-PPy/GR nanocomposite electrode exhibits high output current in comparison to the electrode of PPy and PPy/GR prepared under identical conditions without the presence of a catalyst, indicate enhancement of charge storage in C-PPy/GR. Applying equation (1) to the CV curves for all of the electrodes yields specific capacitances ranging from 797.6 F/g for the 1.0 mM Fe C-PPy/GR, 689.6 F/g for the 0.5 mM Fe C-PPy/GR and 422.9 F/g for the 0.25 mM Fe C-PPy/GR electrodes to 296.9 F/g for the PPy/GR electrode and 157.4 F/g for PPy and 188.5 F/g for C-PPy. This result demonstrates that with only 1.0 mM $FeCl_3$ catalyst, the capacity of the nanocomposite increase more than 4 times compared with PPy film synthesize with and without catalysts, and increase 2.6 times compared with PPy/GR nanocomposite film, which is very efficient and cost-effective. 1.0 mM Fe C-PPy/GR shows the best performance because the PPy morphology obtained after adding suitable amount of

$FeCl_3$ catalyst. As shown by FESEM and elaborated on above, 1.0 mM Fe C-PPy/GR has a higher particle density while still maintaining a relatively low average particle size, leading to a large redox-active surface area able to contribute to the material's pseudocapacitance, at the same time, does not hinder the EDLC performance of GR as the polymeric aggregation is prevented. Through this unique morphology, the contribution of pseudocapacitance from PPy and EDLC from GR are fully harnessed and exhibit superior charge storage performance in supercapacitor application. Conversely, the large and densely pack PPy particle growth of PPy/GR are undesirable for fast ion kinetics and is attributed to the decreased charge storage performance.

Moreover, the CV curves of 1.0mM Fe C-PPy/GR with various scan rates are illustrated in Fig.8B. In the CV curves, the current density is increased with increasing scan rates, but does not indicate a greater charge capacitance at high scan rate. This can be attributed to the greater charge mobilization per unit time, where the increase of scan rate will lead to reduced of effective interaction between the ions and the electrode and the deviation from rectangularity of the CV become obvious at a scan rate of 50 and 100 mV/s.

Galvanostatic charge/discharge as illustrated in Fig. 9 are obtained at the current density of 1 A/g between -0.2 and 0.8 V versus Ag/AgCl in 1 M $NaSO_4$ for PPy, C-PPy, PPy/GR and 1.0 mM Fe C-PPy/GR. Near-ideal EDLC behavior of the charge/discharge curves is seen by the symmetry of the charge and discharge slopes, where a triangle curve is observed. All of the curves illustrated in Fig. 9 are not ideal straight lines, indicating the involvement of a Faradaic reaction process of the PPy. Although the discharge curve of PPy/GR and 1.0 mM Fe C-PPy/GR are quite similar to each other,

the curvatures become more pronounced for 1.0 mM Fe C-PPy/GR compared with PPy/GR, indicating the increased contribution of pseudo capacitance to the systems.

Electrochemical impedance spectroscopy (EIS) is performed to investigate the mechanistic aspect for different nanostructures of PPy/GR electrode. The EIS data were analyzed using Nyquist plot; a plot of the imaginary component (Z") of the impedance against the real component (Z'). Nyquist plots of nanocomposites in the frequency range (100 KHz to 10 mHz) are shown in Fig. 10. A typical Nyquist plot of an ideal capacitor shows a small semicircle at high-medium frequency presented in the lower left portion of the spectra followed by a straight line in the low frequency region. All EIS plots in Fig. 10 are shown to exhibit a straight line at low frequencies, indicating a pure capacitive behavior, representative of the ion diffusion in the electrode structure. Insets in Fig. 10 shows magnified high frequency region of nanocomposite. The impedance curves of PPy/GR and 1.0 mM Fe C-PPy/GR show a distorted and unobvious semi-circle in the high-medium frequency region is attributable to good electronic conductivity of PPy/GR nanocomposite films. The first intercept point of the semi-circle on the real axis represents equivalent series resistance (ESR). This corresponds to the total resistance due to resistance from the electrolyte, internal resistance of electrode and the contacts between the electrode and the current collector. The diameter of the semi-circle at medium frequency is associated with the double layer capacitance and charge transfer resistance (Rct). The Rct is a resistance due to different conductivity in the nanocomposite (electronic conductivity) and the aqueous electrolyte phase (ionic conductivity). So the resistance arises due to discontinuities in the charge transfer process at the electrode/electrolyte interface. This forms an activation barrier (also

called kinetic regime) that limits the migration of charge-complexes. Fig. 9 shows the ESR and charge transfer resistance for 1.0 mM Fe C-PPy/GR (ESR = 21.7 Ω and Rct = 0.7 Ω) nanocomposite was much lower than that of PPy/GR (ESR = 31.3 Ω and Rct = 0.9 Ω) nanocomposite. Contributing factor in this higher resistance observed in PPy/GR include electrolyte diffusion resistance and charge transfer resistance owing to pseudocapcitive materials. The present of polymeric agglomeration blocking electrolyte channel can be expected to increase the diffusion resistance as well as the charge transfer resistance of the redox reaction. These results clearly show that the lower resistance of the 1.0 mM Fe C-PPy/GR attribute to a change in the morphology and structure of individual GR sheets. Open structures of GR sheets provide easier access (less resistance) for the intercalation and de-intercalation of charges compare with a flat and dense layer of GR in PPy/GR leading to low ESR of 1.0 mM Fe C-PPy/GR nanocomposite. The charge transfer resistance for the 1.0 mM Fe C-PPy/GR is much lower than that of PPy/GR electrodes, indicating more efficient charge transfer kinetics compared to PPy/GR.

Furthermore, electrochemical stability is one of the crucial factors to supercapacitors electrode for any practical used. Fig. 11 shows the cycling performances of the two nanocomposites at 1 A/g by galvanostatic charge/discharge test. The specific capacitance of 1.0 mM Fe C-PPy/GR decreases by ~25 % while that of PPy/GR decreases by ~11% after 1000 cycles. Even though the percentage of specific capacitance retention of 1.0 mM Fe C-PPy/GR is lower, its specific capacitance (554 F/g) is still twofold higher than that of PPy/GR (260 F/g). It is interesting to note that the PPy/GR electrode is much more stable than that for C-PPy/GR. This implies

that incorporation of PPy onto GR sheets had a significant influence on the cycling durability of the electrodes during cycling charge/discharge process. Within the nanocomposite, GR sheets acted as interconnectors for improving the internal electrical conductivity and enhancing the specific surface area of the electrodes for EDLC charge storage. Meanwhile, the PPy acted as frameworks to bridge the GR sheets and prevent GR sheets from severe swelling and shrinking during the cycling process. Although reducing particle size of PPy in 1.0 mM Fe C-PPy/GR exhibits impressive charge storage performance, however, the frameworks of nanocomposite are weakened due to disappearing of thick PPy coating and it may undergo serious structural alteration during the charge/discharge process leading to fast decrease of specific capacity retention.

Experimental Setup

Materials Required

Graphite powder is obtained from Ashbury Graphite Mills Inc., code no. 3061. Sulphuric acid (H_2SO_4, 95–98%), phosphoric acid (H_3PO_4, 85%), potassium permanganate ($KMnO_4$, 99.9%), and hydrogen peroxide (H_2O_2, 30%) is purchased from Systerm. Hydrogen chloride (HCl, 37%) and iron (III) chloride ($FeCl_3$, 98%) is purchased from Sigma-Aldrich. Pyrrole (99%, Acros organic) is stored at 0 ^{0}C and distilled prior to use. Sodium p-toluenesulfonate (NapTS, 70 %) is purchased from Fluka.

Preparation of GO

GO is synthesized using the simplified Hummer's method. Graphite oxide is obtained by oxidation of 3 g of graphite flakes with H_2SO_4:H_3PO_4 (360:40 ml) and 18 g of $KMnO_4$. 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, H_2O_2 solution is 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 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 and step of terminating oxidation of the graphite oxide solution is performed by adding hydrogen peroxide.

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 one embodiment of the present invention, the step of applying the electric field includes providing an electrophoresis solution includes a supporting electrolyte, and forming the graphene-based conducting nanocomposite film on a surface of the substrate.

Particularly, the nanocomposite film is formed on the surface of the substrate by simultaneously depositing the at least one portion of the deposition solution and the 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 one embodiment of the present invention, the step of forming of the nano-composite film includes electro-chemical processing and the time period is about 30 minutes to allow polypyrrole to form in the deposition solution.

Preparation of C-PPy/GR nanocomposite

PPy/GR nanocomposite films are synthesized by catalyst-assisted electrochemical polymerization from an aqueous solution placed in a one-compartment cell. The deposition solution contained 0.1 M pyrrole, 1mg/ml GO, 0.1 M NapTS and 0.25-1.0 mM $FeCl_3$, and the solution is vigorously stirred for 30 minutes to allow PPy to form in the solution. The concentration of $FeCl_3$ is kept low to ensure that the polymer is doped primarily with pTS^- ions. The solution is then transferred to deposition cell, and PPy/GR is deposited at a constant potential of +0.8 V using potentiostat-galvanostat (Elchema model EQCN-502 Faraday cage) 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 and all the potentials are referred to the saturated calomel electrode (SCE). The time of polymerization is about 2 hours. For comparison, a 0.1 M PPy/GR nanocomposite film

without catalyst is synthesized and 0.1 M PPy film is synthesized with and without catalyst.

Experimentation:

Characterization of Materials:

The surface morphology of GO, PPy, C-PPy, PPy/GR and C-PPy/GR is investigated using field emission scanning electron microscopy (FESEM, FEI Nova NanoSEM 400). High resolution transmission electron microscopy (HRTEM) is carried out using a JEOL JEM-2100 F. The crystalline structure of the samples is analyzed using Siemens D5000 X-ray diffraction (XRD). Raman spectra is measured using a Renashaw's inVia Raman microscope with a 532 nm laser and FT-IR spectra are recorded on a Perkin-Elmer model 1725x.

Electrochemical measurements:

To understand the electrochemical performance of the nanocomposite electrode, the electrochemical properties of the materials are measured using the VersaSTAT 3 electrochemical system (Princeton Applied Research). Cyclic voltametry (CV), galvanostatic charge/discharge and electrochemical impedance spectroscopy (EIS) are all carried out in a three-electrode cell system, including nanocomposite films as the working electrode, platinum wire as a counter electrode and Ag/AgCl as the reference electrode, is employed to conduct the experiment. CV was carried out at between -0.2 and 0.8 V (versus Ag/AgCl) at scan rates between 2 and 100 mV/s. The specific capacitance values of the samples are calculated from cyclic voltammograms using Equation (1).

$$Cm = \frac{\int i}{m*S} \qquad \text{Equation (1)}$$

where Cm 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. Galvanostatic charge/discharge are carried out between -0.2 and 0.8 V (versus Ag/AgCl) at a current density of 1 A/g and the long term cycling performance of the PPy/GR and 1.0 mM Fe C-PPy/GR electrodes are measured by the consecutive galvanostatic charge-discharge at a current density of 1 A / g for 1000 cycles. An EIS is carried out between 100 KHz to 10 mHz with an ac amplitude of 5mV.

Therefore, as may be seen, the present invention provides a simple method for preparing polypyrrole and graphene nanocomposite films using a catalyst-assisted electrochemical deposition method with significantly enhance charge storage performance. Particularly, the present invention evidently illustrates that by FESEM that the particle size of PPy is able to be controlled using different catalyst amount and nano-sized PPy is formed with 1.0 mM of FeCl3 as a catalyst. Moreover, in stark contrast without the catalyst, PPy in nano-sized dimension that could not be formed as elongation instead of nucleation of PPy occurred. This explains the formation of a thick layer PPy in the nanocomposite in the absence of the catalyst.

The PPy decorated graphene enabled the efficient transfer of electrons as well as ions within the matrix of the nanocomposite. The specific capacitance of as obtained C-PPy/GR is high as 797.6 F/g and the impressive performance of C-PPy/GR is attributed to the unique morphology of C-PPy/GR allowed the pseudo capacitance of PPy and EDLC of GR to be fully harnessed. The present invention provides one or advantages stated above and the catalyst-assisted electrochemically synthesize C-PPy/GR nanocomposite is a promising candidate for high performance supercapacitors.

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 polypyrrole and graphene nanocomposite films, said method comprising the steps of:

providing a graphite source and oxidizing said graphite source to form graphite oxide solution;

washing said graphite oxide solution for thickening said 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;

introducing at least one reagent into an one-compartment cell;

providing a deposition solution and dipping it in said graphite oxide gel;

stirring said deposition solution for a particular time period;

reacting said at least one reagent to form polypyrrole within said deposition solution;

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 to form polypyrrole and graphene nanocomposite films.

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 and step of terminating oxidation of said graphite oxide solution is performed by adding hydrogen peroxide.

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 and said time period is about 30 minutes to allow polypyrrole to form in said deposition solution.

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

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 1, wherein said reagent comprises metal catalyst and said metal catalyst is Iron (III) chloride.

10. The method of claim 5, wherein said conductive polymer is a polypyrrole and a supporting electrolyte is a sodium p-toluenesulfonate.

11. The method according to claim 1, wherein said substrate has an active surface and said active surface is conductive.

12. The method according to claim 11, wherein said active surface is selected from graphite, Indium-Tin-Oxide (ITO), glass, which may or may not be coated with a metal.

13. The method according to claim 12, wherein said active surface is selected from an electrode and a metal (or alloy) coated glass.

14. The method of claim 1, wherein said liquid is an acid solution and said acid solution is hydrochloric acid.

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

16. The method of claim 1, wherein said deposition solution comprises at least one of a polypyrrole of about 0.1 M , about 1 mg/ml of graphite oxide gel, about 0.1 M of sodium p-toluenesulfonate, and about 0.25-1.0 mM of Iron (III) chloride.

17. 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.

18. A catalyst-assisted polypyrrole/graphene nanocomposite film, said nanocomposite film prepared by a method comprising the steps of:

providing a graphite source and oxidizing said graphite source to form graphite oxide solution;

washing said graphite oxide solution for thickening said 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;

introducing at least one reagent into an one-compartment cell;

providing a deposition solution and dipping it in said graphite oxide gel;

stirring said deposition solution for a particular time period;

reacting said at least one reagent to form polypyrrole within said deposition solution;

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 to form polypyrrole and graphene nanocomposite films.

19. The catalyst-assisted polypyrrole/graphene nanocomposite film of claim 18, wherein said nancomposite film prepared by a method comprising the steps of:

exfoliating said graphite oxide in said liquid by repeatedly washing with de-ionized water;

performing termination of oxidation of said graphite oxide solution by addition of hydrogen peroxide;

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.

20. The catalyst-assisted polypyrrole/graphene nanocomposite film of claim 19, wherein said nanocomposite film prepared by a method comprising the steps of:

forming of said nano-composite film comprises electro-chemical processing and said time period is about 30 minutes to allow polypyrrole to form in said deposition solution; 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.

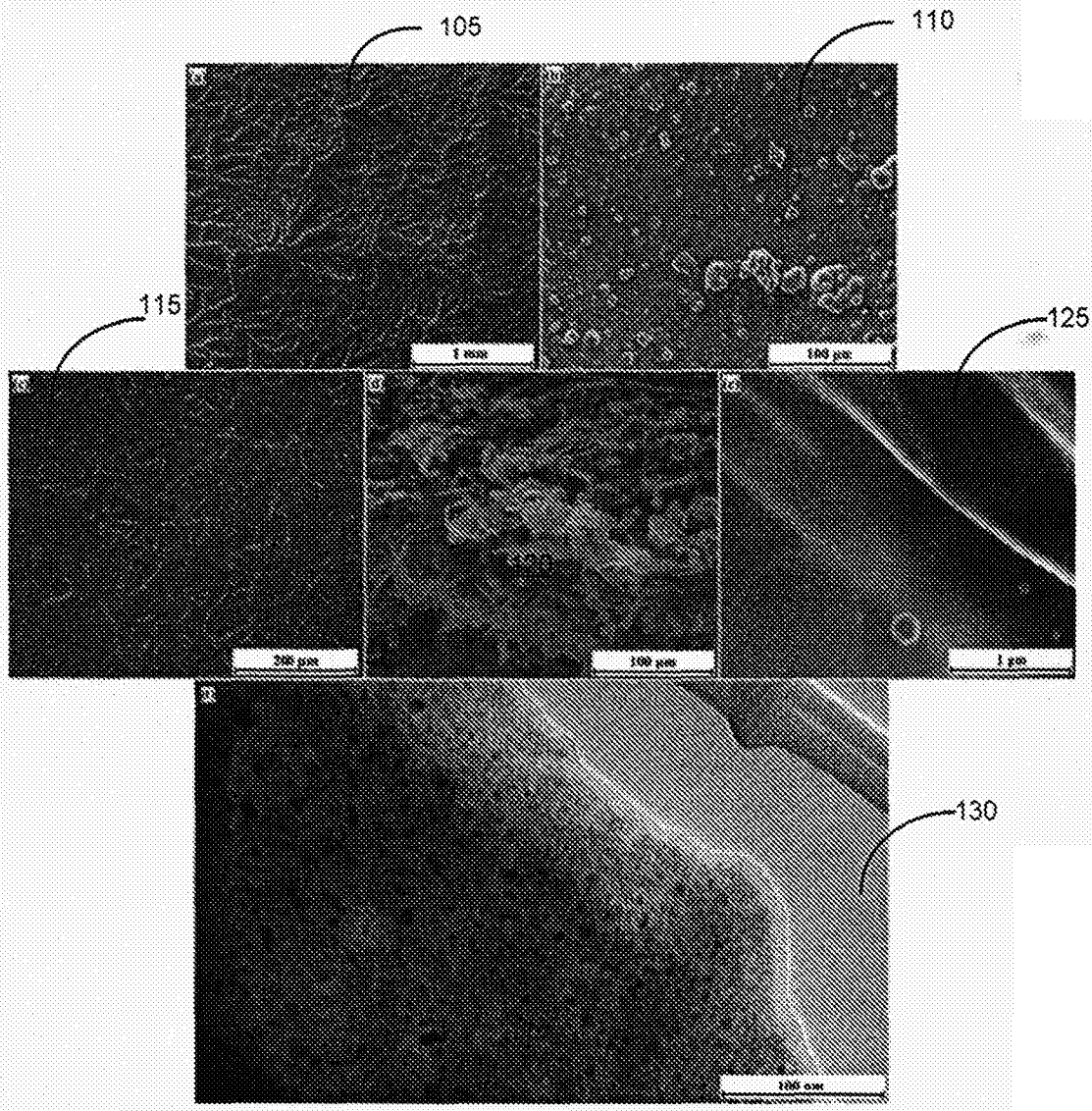

FIG. 1

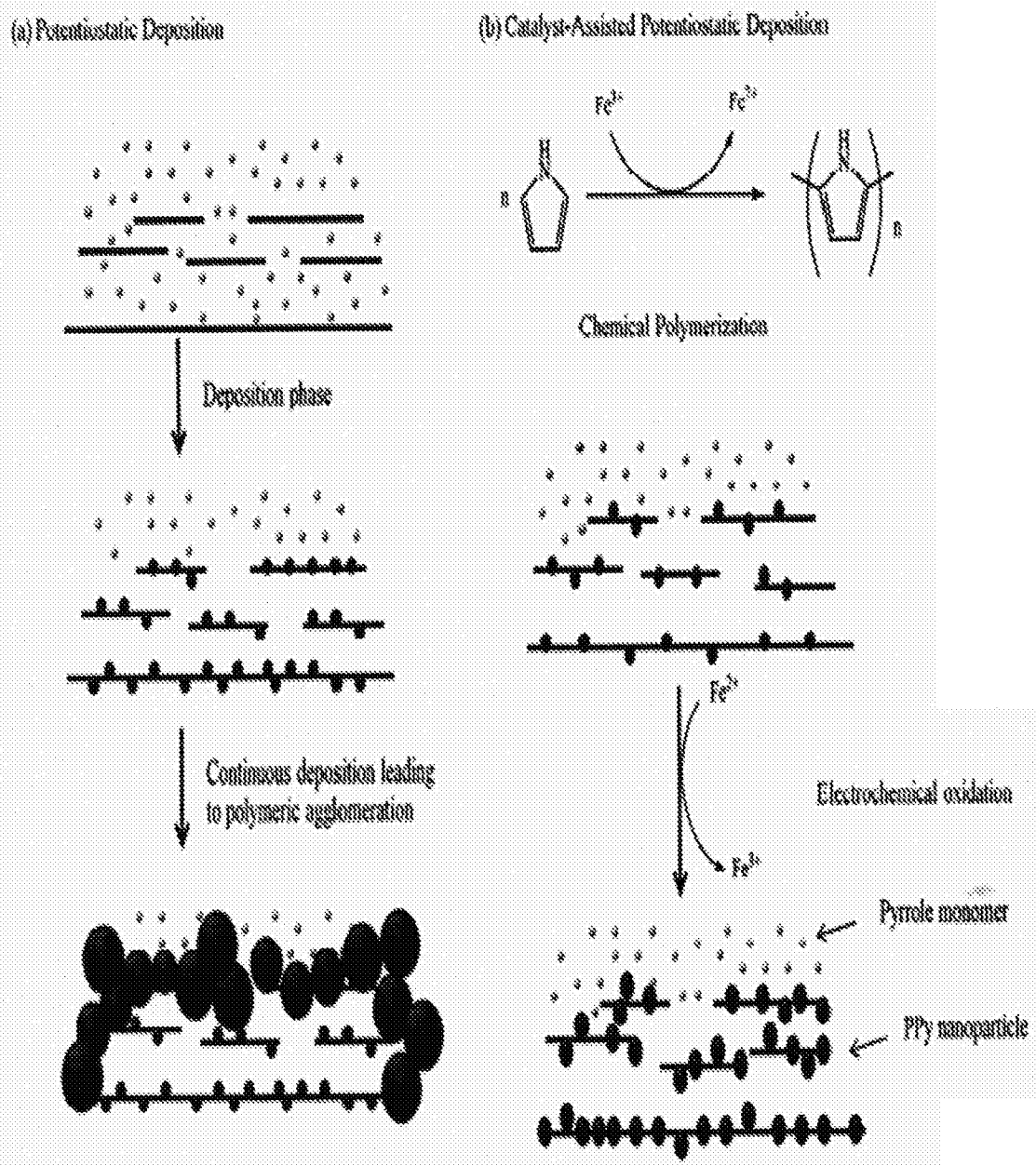
(a) Potentiostatic Deposition
Deposition phase
Continuous deposition leading to polymeric agglomeration
(b) Catalyst-Assisted Potentiostatic Deposition
Chemical Polymerization
Electrochemical oxidation
Pyrrole monomer
PPy nanoparticle

FIG. 2

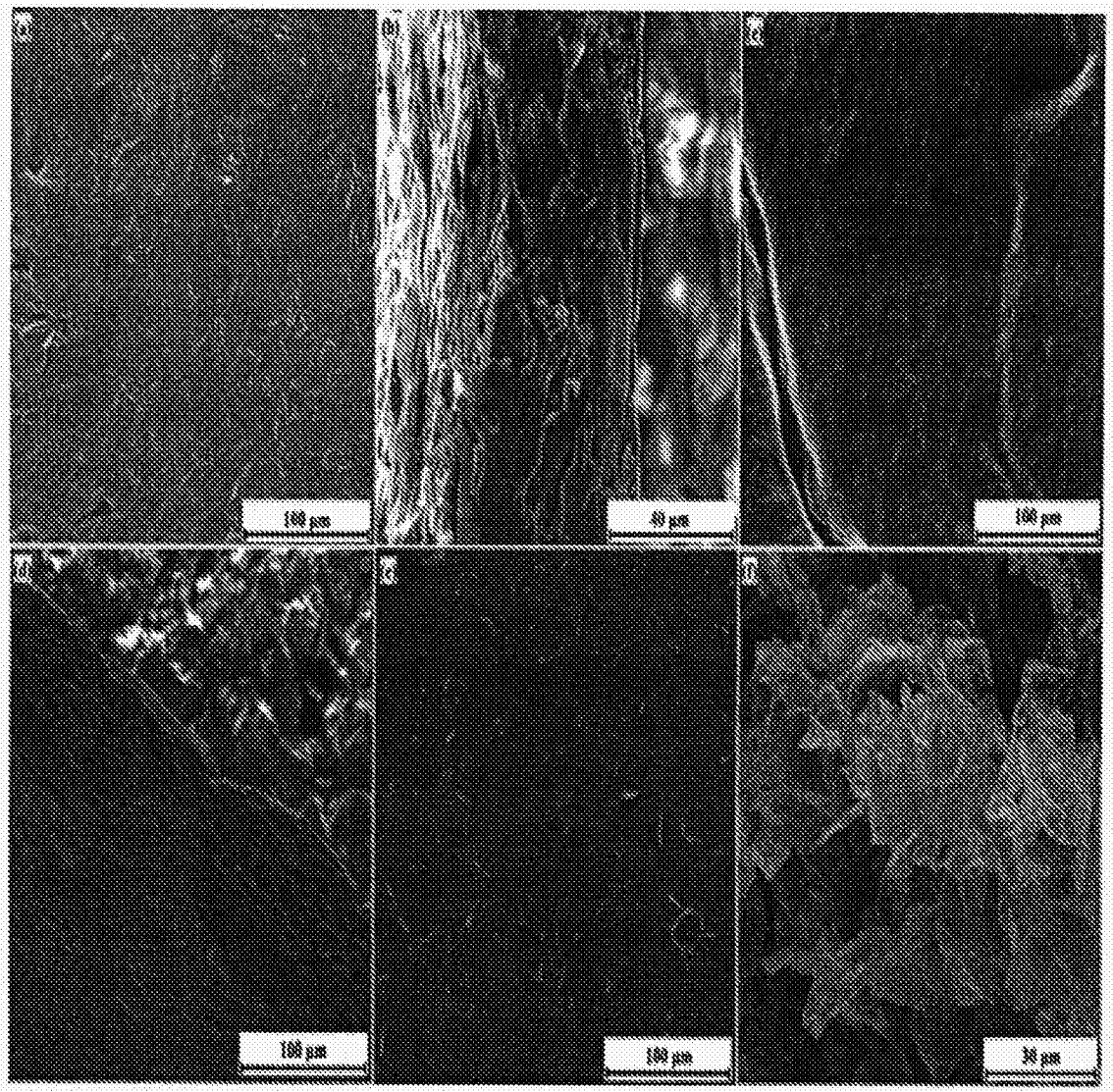

FIG. 3

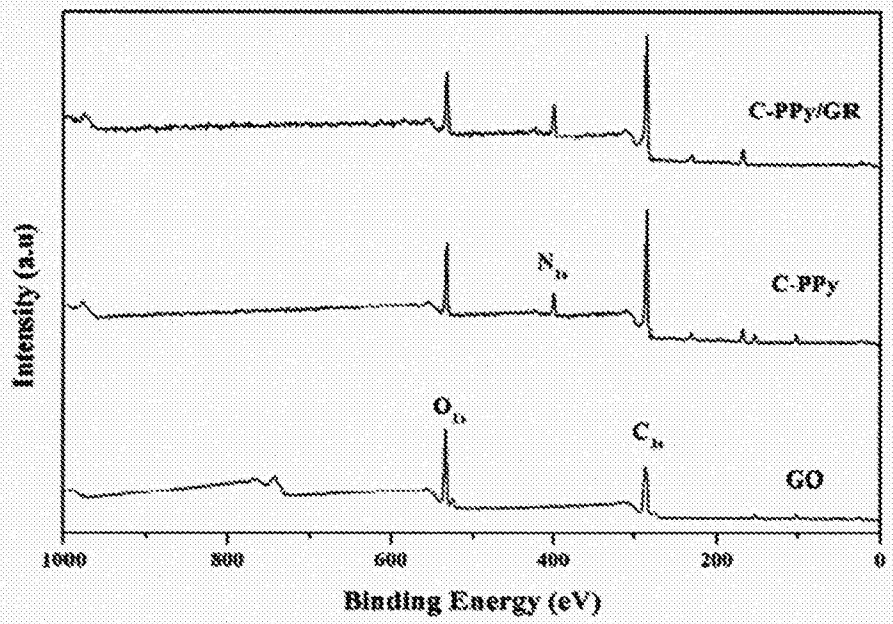
C-PPy/GR
C-PPy
GO
Intensity (a.u)
Binding Energy (eV)
1000
800
600
400
200
0

FIG. 4A

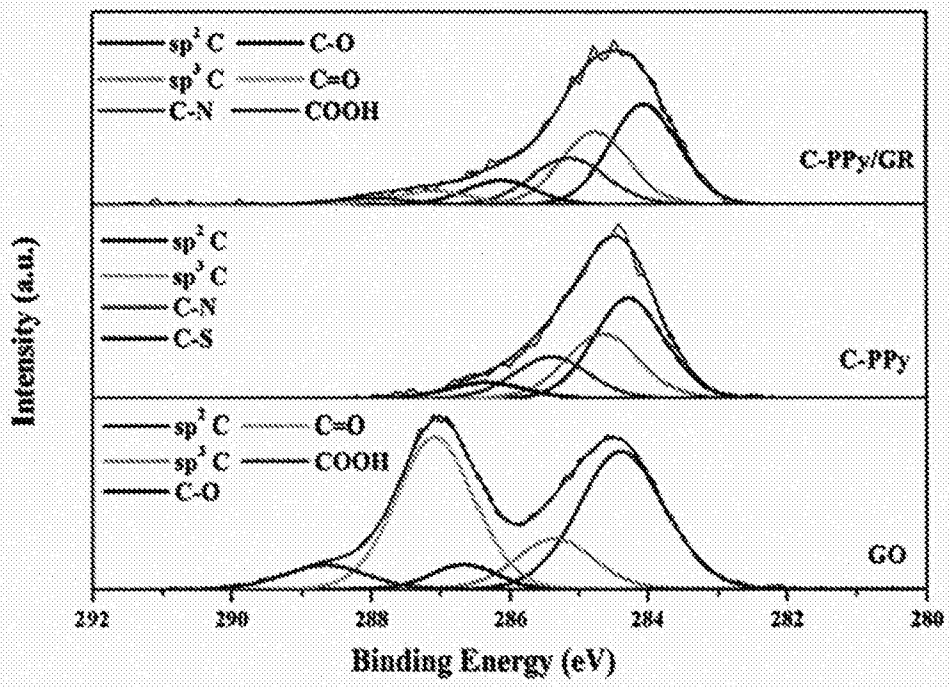
sp² C
C-O
sp³ C
C=O
C-N
COOH
C-PPy/GR
sp² C
sp³ C
C-N
C-S
C-PPy
sp² C
C=O
sp² C
COOH
C-O
GO
Intensity (a.u.)
292
290
288
286
284
282
280
Binding Energy (eV)

FIG. 4B

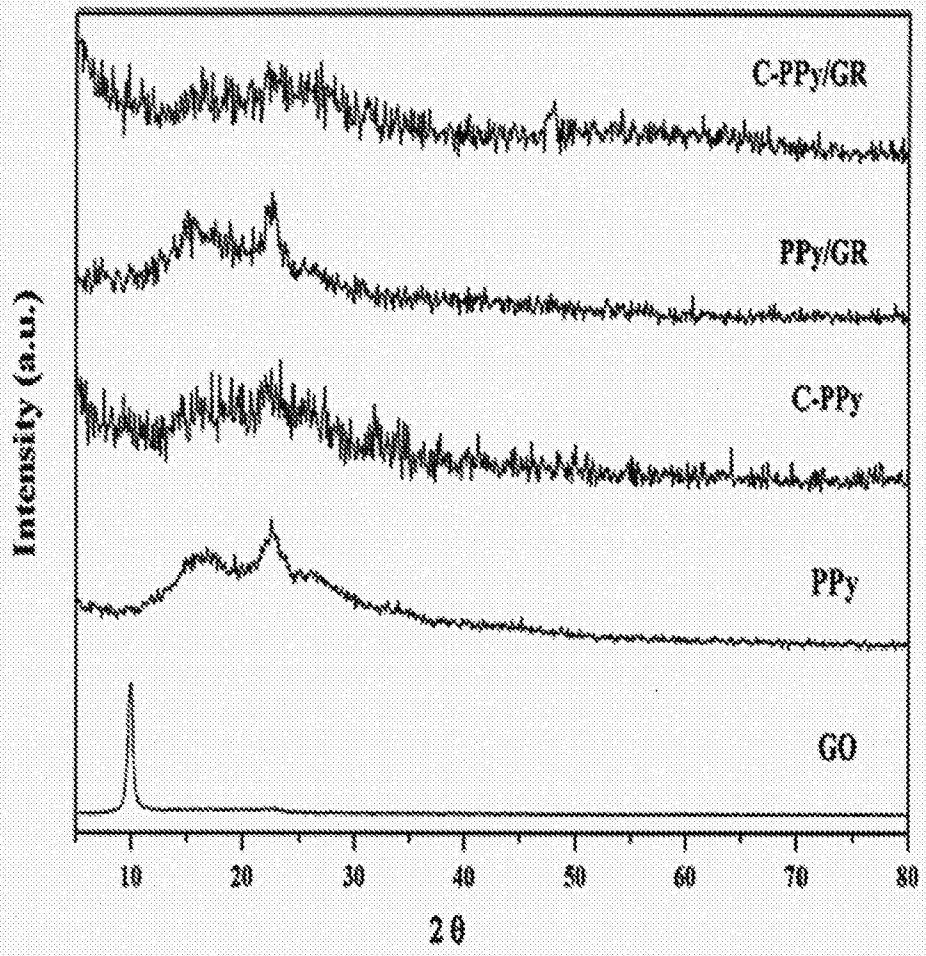

FIG.5

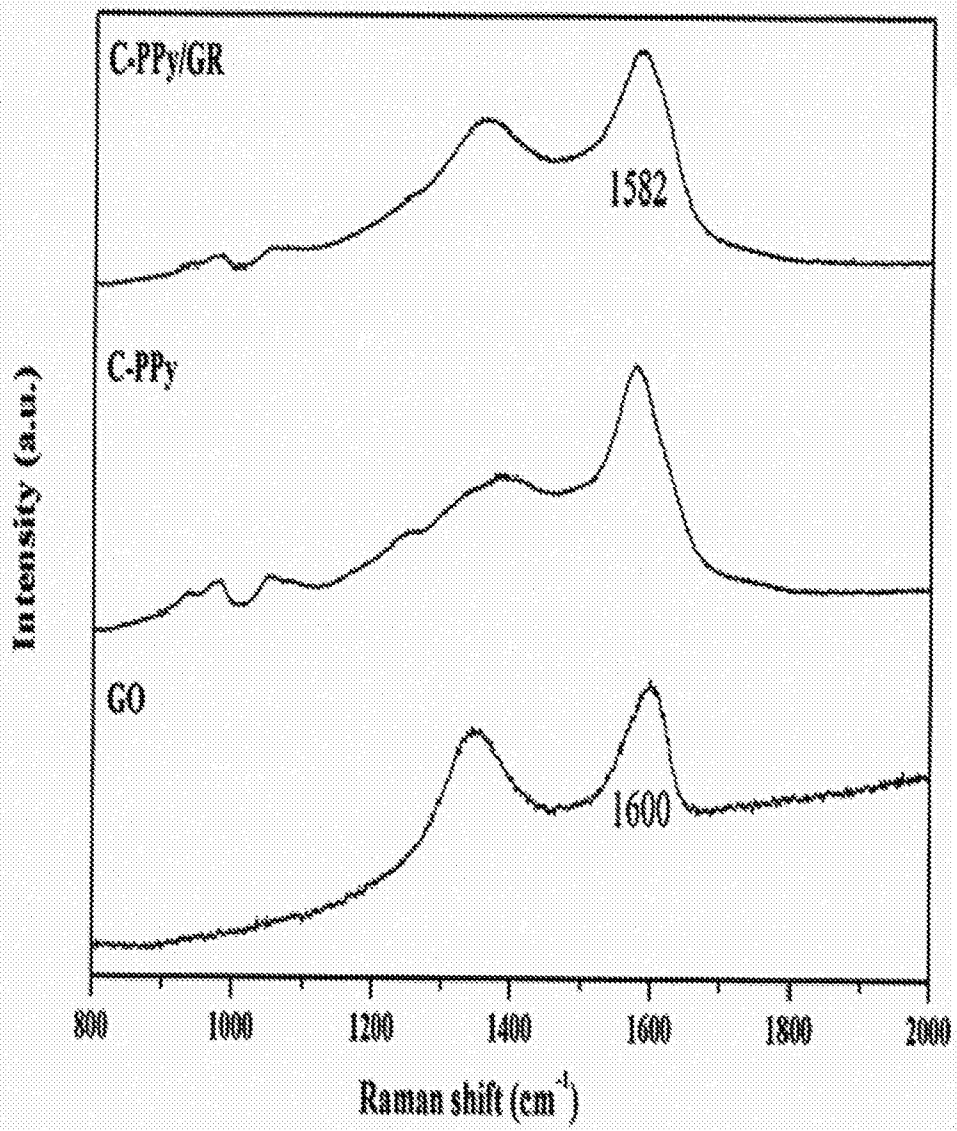
C-PPy/GR
1582
C-PPy
GO
1600
Intensity (a.u.)
800
1000
1200
1400
1600
1800
2000
Raman shift (cm-1)

FIG.6

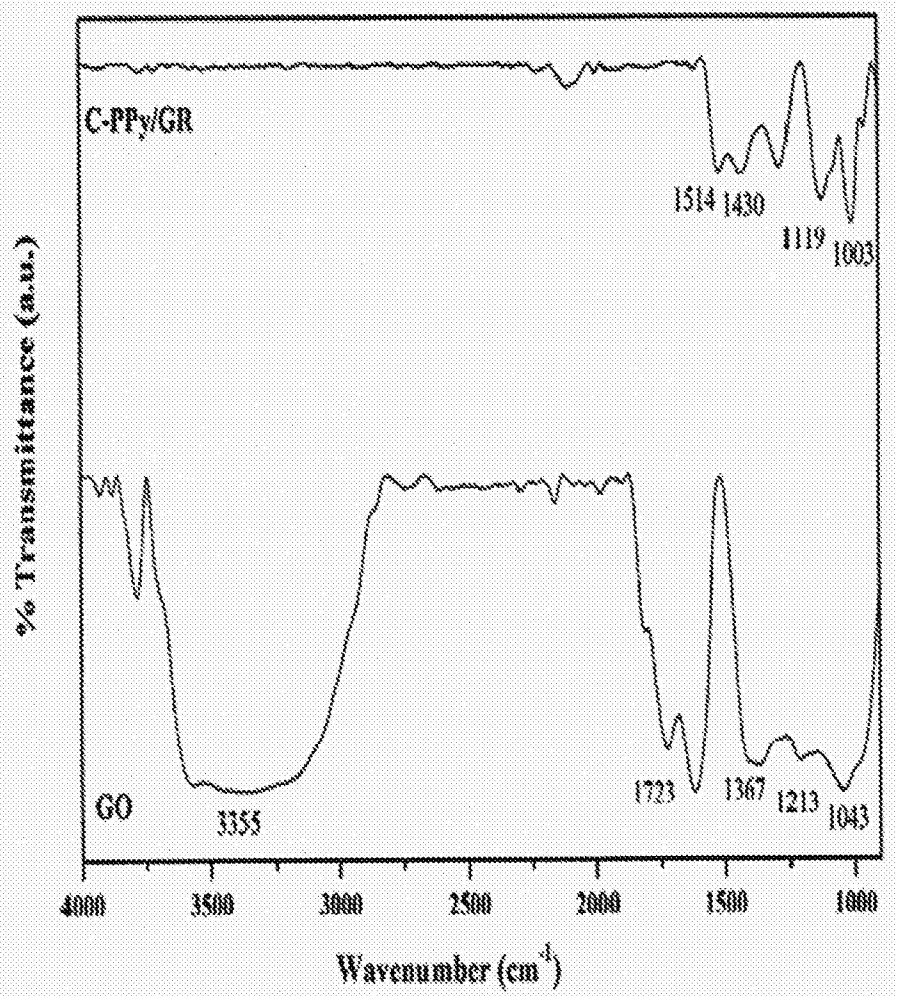
C-PPy/GR
1514
1430
1119
1003
GO
3355
1723
1367
1213
1043
% Transmittance (a.u.)
4000
3500
3000
2500
2000
1500
1000
Wavenumber (cm-1)

FIG. 7

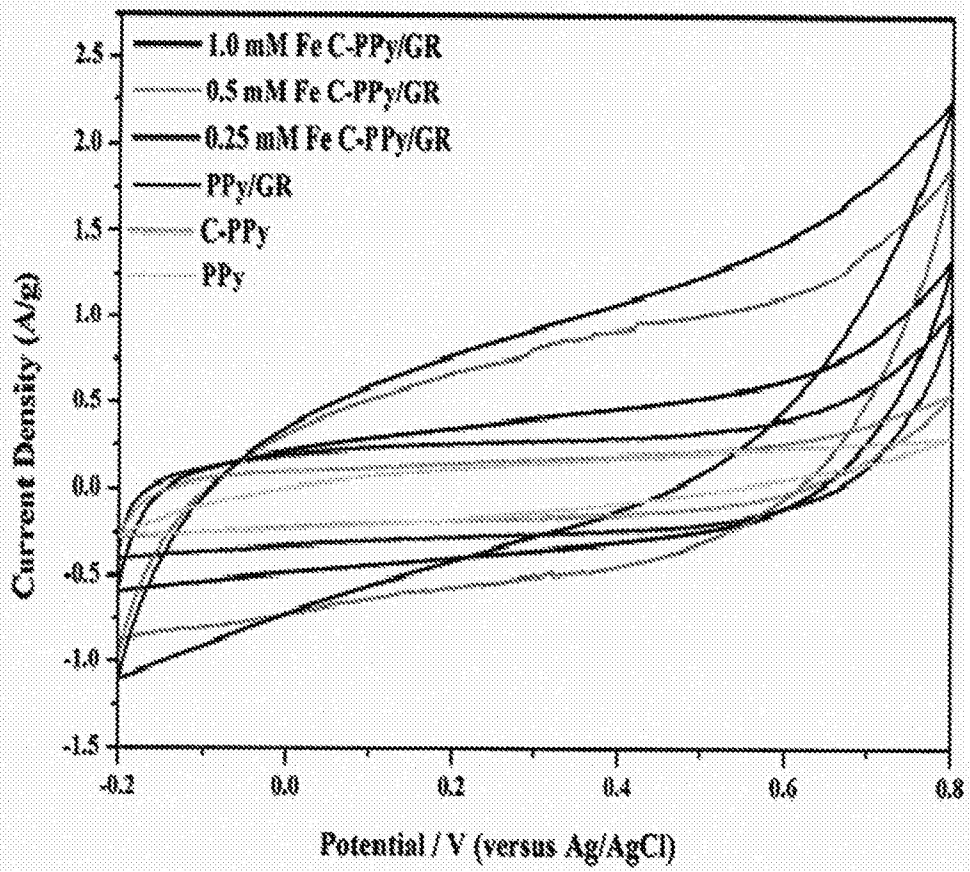
1.0 mM Fe C-PPy/GR
0.5 mM Fe C-PPy/GR
0.25 mM Fe C-PPy/GR
PPy/GR
C-PPy
PPy
Current Density (A/g)
Potential / V (versus Ag/AgCl)
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
-0.2
0.0
0.2
0.4
0.6
0.8

FIG. 8A

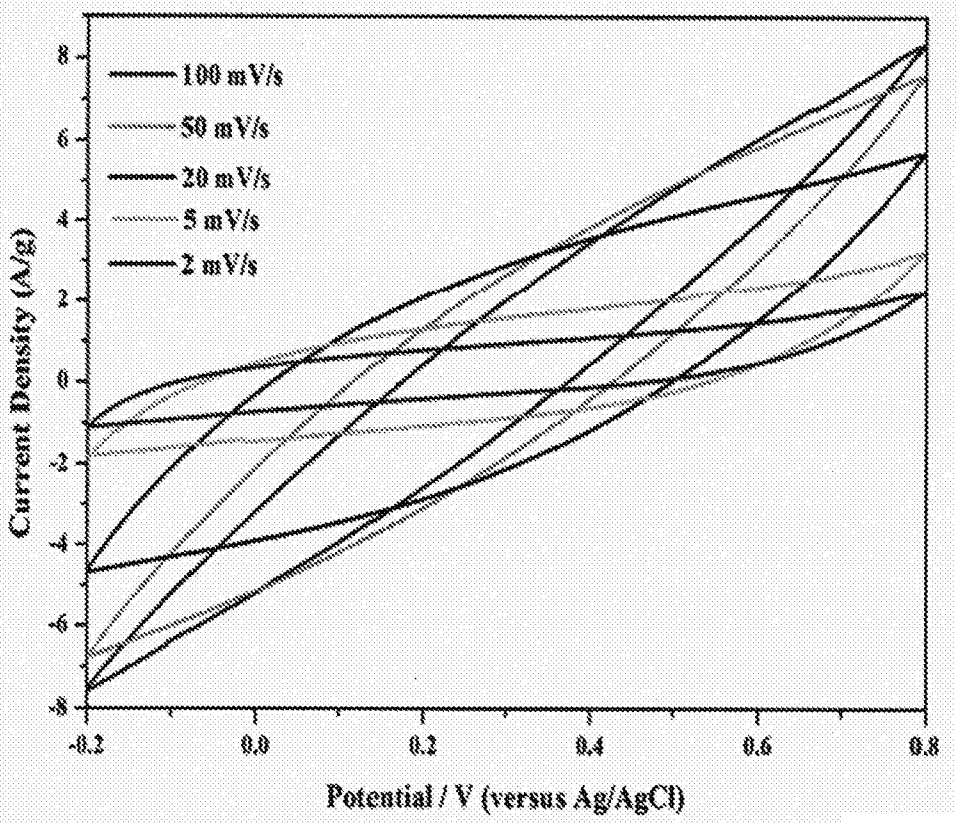
100 mV/s
50 mV/s
20 mV/s
5 mV/s
2 mV/s
Current Density (A/g)
Potential / V (versus Ag/AgCl)
8
6
4
2
0
-2
-4
-6
-8
-0.2
0.0
0.2
0.4
0.6
0.8

FIG. 8B

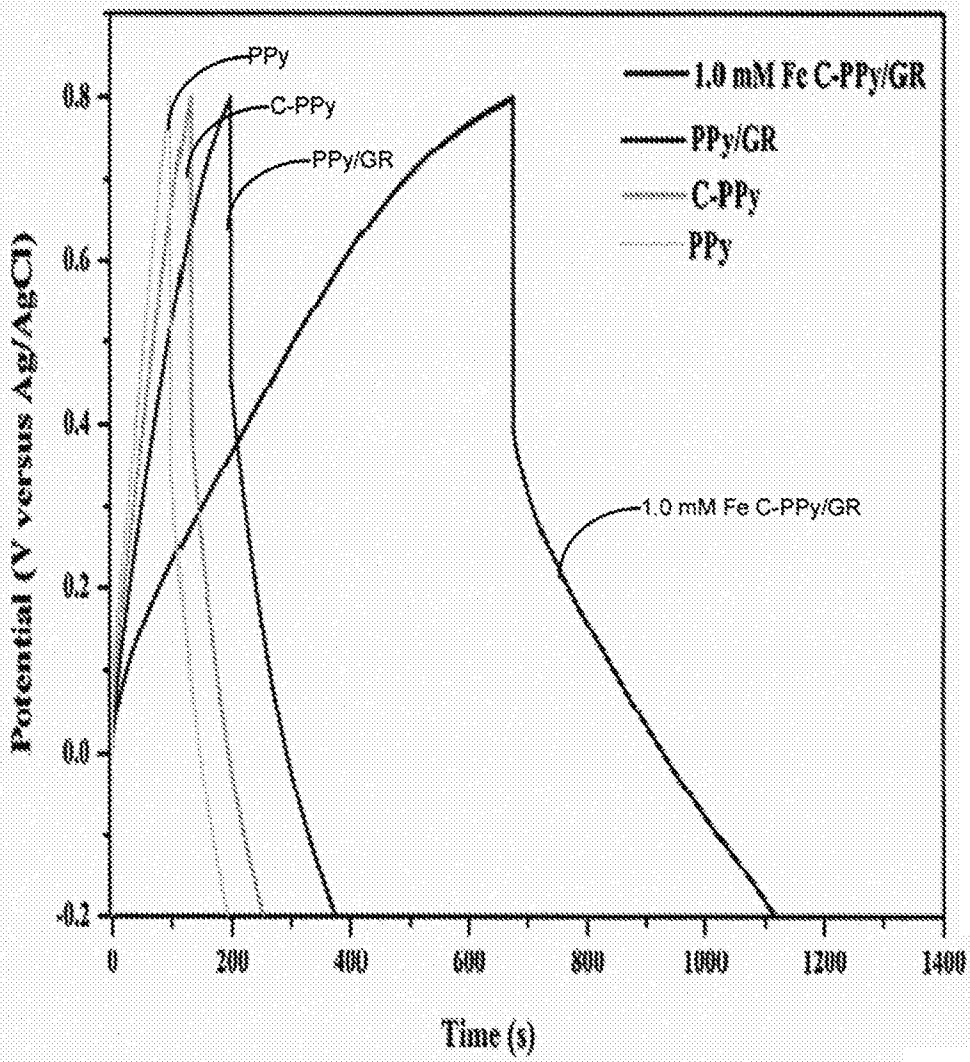
PPy
C-PPy
PPy/GR
1.0 mM Fe C-PPy/GR
PPy/GR
C-PPy
PPy
1.0 mM Fe C-PPy/GR
Potential (V versus Ag/AgCl)
0.8
0.6
0.4
0.2
0.0
-0.2
0
200
400
600
800
1000
1200
1400
Time (s)

FIG. 9

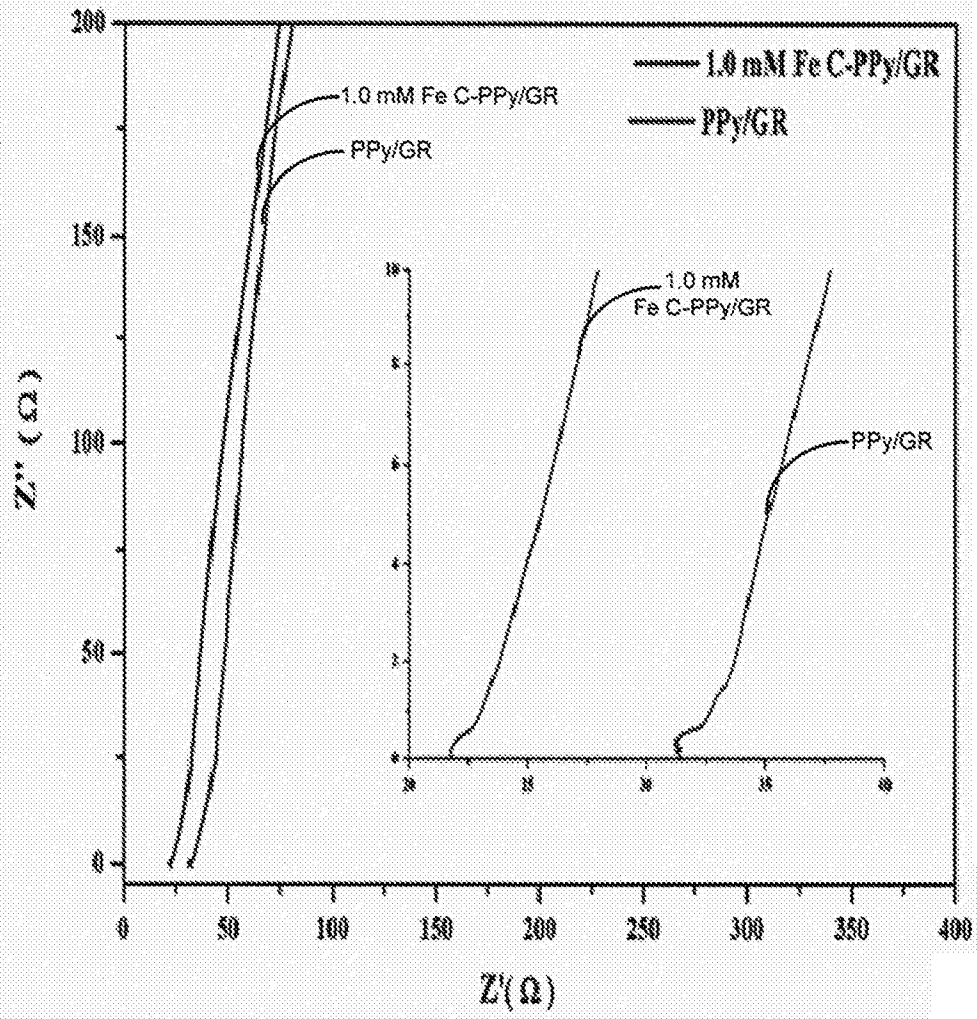
1.0 mM Fe C-PPy/GR
PPy/GR
1.0 mM Fe C-PPy/GR
PPy/GR
1.0 mM
Fe C-PPy/GR
PPy/GR
Z'' (Ω)
Z'(Ω)
0
50
100
150
200
250
300
350
400

FIG. 10

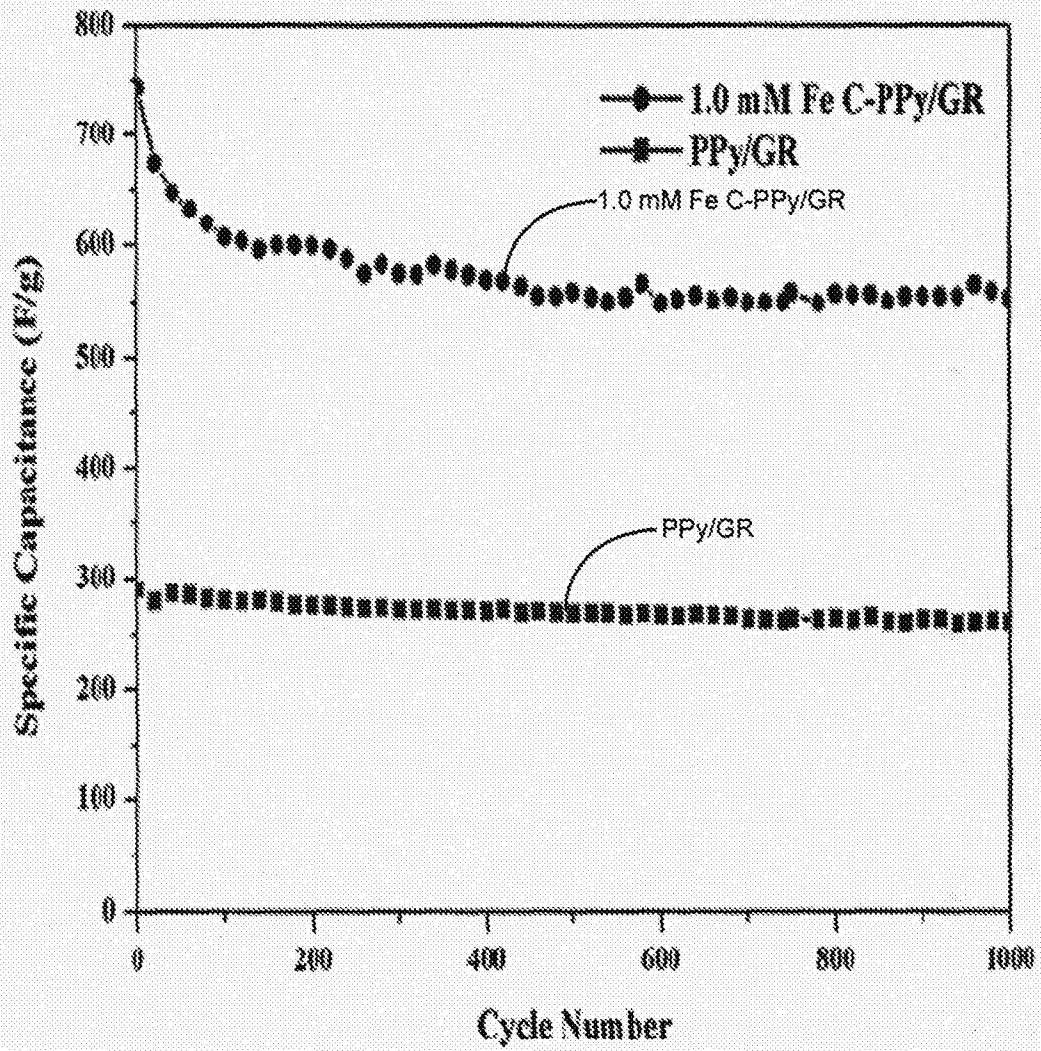
1.0 mM Fe C-PPy/GR
PPy/GR
1.0 mM Fe C-PPy/GR
PPy/GR
Specific Capacitance (F/g)
Cycle Number
800
700
600
500
400
300
200
100
0
0
200
400
600
800
1000

FIG. 11

INTERNATIONAL SEARCH REPORT

International application No.
PCT/MY2014/000054

A. CLASSIFICATION OF SUBJECT MATTER

Int.Cl. C01B31/02(2006.01)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)

Int.Cl. C01B31/02

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

Published examined utility model applications of Japan 1922-1996
Published unexamined utility model applications of Japan 1971-2014
Registered utility model specifications of Japan 1996-2014
Published registered utility model applications of Japan 1994-2014

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

JSTPlus/JMEDPlus/JST580(JDreamIII)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2010-18696 A (TORAY INDUSTRIES, INC.) 2010.01.28, entire text (Family: none)	1-20
A	JP 2013-87023 A (KRI, Inc.) 2013.05.13, entire text (Family: none)	1-20
A	WO 2013/089026 A1 (PANASONIC CORPORATION) 2013.06.20, entire text (Family: none)	1-20
A	C. BORA, S.K. DOLUI, "Fabrication of polypyrrole/graphene oxide nanocomposites by liquid/liquidinterfacial polymerization and evaluation of their optical, electrical and electrochemical properties", Polymer, 2012.01.10, Volume 53, Issue 4, Pages 923-932	1-20

☐ 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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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
14.08.2014	26.08.2014

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