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(54) **Title:** HIGH SURFACE AREA NANO-STRUCTURED GRAPHENE COMPOSITES AND CAPACITIVE DEVICES INCORPORATING THE SAME

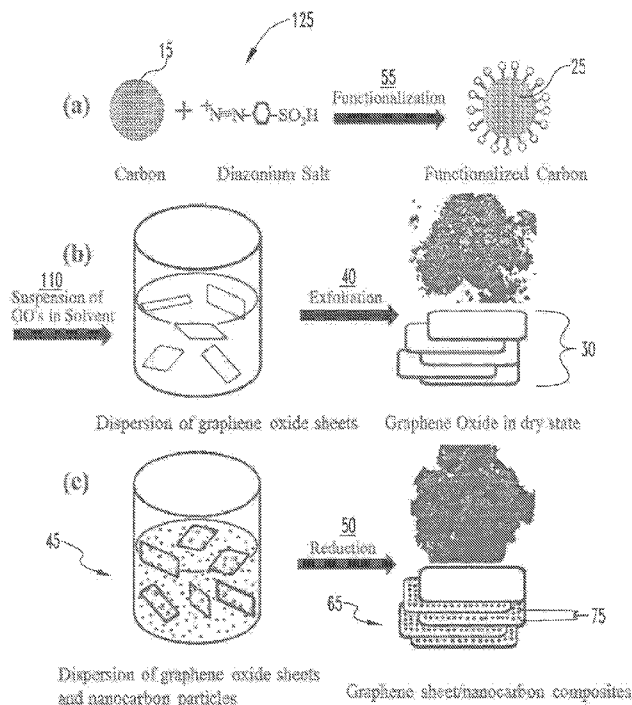


Fig. 1

(57) **Abstract:** A carbon composite material, including a plurality of spaced graphene sheets, each respective sheet having opposed generally planar surfaces, and a plurality of functionalized carbonaceous particles. At least some functionalized carbonaceous particles are disposed between any two adjacent graphene sheets, and each respective at least some functionalized carbonaceous particle is attached to both respective any two adjacent graphene sheets. Each respective graphene sheet comprises at least one layer of graphene and at least portions of respective any two adjacent graphene sheets are oriented substantially parallel with one another.



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HIGH SURFACE AREA NANO-STRUCTURED GRAPHENE COMPOSITES AND CAPACITIVE DEVICES INCORPORATING THE SAME

TECHNICAL FIELD

The novel technology relates generally to materials science, and, more particularly, to a high surface area graphene composite material.

BACKGROUND

Graphene, a single-atom-thick sheet consisting of sp^2 hybridized carbon atoms arrayed in a honeycomb pattern, is the building block of graphitic carbons. Graphene may be viewed as an individual atomic plane of the graphite structure. Graphene as a two-dimensional nanosheet has attracted increasing interest due to its unique properties of high in-plane electronic conductivity, high tensile modulus, and high surface area, which make graphene an attractive candidate for applications in electronic devices and composite materials. Moreover, with its high surface area and good chemical stability, graphene may be used as a gas adsorbant,

ultracapacitor material, or a supporting material for developing novel heterogeneous catalysts with enhanced catalytic activity.

Graphene may be produced by any one of several methods, including the straightforward exfoliation technique of manually peeling off of the top surface of small mesas of pyrolytic graphite, chemical vapor deposition on metal surfaces, epitaxial growth on electrically insulating surfaces, such as SiC, and the like. Although multiple production methods do exist, large-scale applications of graphene require simple and cost effective methods of production. Hence, the primary route in making graphene is still the exfoliation of graphite oxides followed by a chemical reduction.

In aqueous solvent dispersions of graphene prepared by chemical reduction, graphene sheets are separated by solvents stabilized by electrostatic forces associated with ionizable groups introduced during the exfoliation. However, like other dispersions of nanomaterials with high aspect ratios, after the solvent is removed from the dispersion, the dried graphene sheets (GSs) usually aggregate and form an irreversibly interconnected or tangled precipitated agglomerate. This agglomeration is driven by the van der Waals interactions between the neighboring graphene sheets, urging the graphene sheets to stack back together in a disorganized and typically haphazard fashion. This agglomeration also leads to a considerable loss of the effective surface area of graphene, which affects the graphene applications in, for example, supercapacitors, batteries, and catalyst supports, where a high surface area of active materials is desired for performance.

Therefore, how to achieve the intrinsically ultra-high surface area of graphene in its solid state is of interest in advancing the applications of graphene materials.

Anchoring nanoparticles on the graphene surface before the GS's aggregation is one effective way to keep the GS's high surface area. The deposition of Pt nanoparticles on a graphene surface before drying has been shown to increase the surface area of the composite from 44 m²/g to 862 m²/g with the anchoring of the Pt nanoparticles on the surface. Graphene polyoxometalate nanoparticle composites have been observed to yield a graphene surface area of about 680 m²/g. Graphene sheet/RuO₂ composites have been observed with increased surface area increases from 108 m²/g to 281 m²/g. These composites also exhibited a high specific capacitance 570 F/g and an enhanced rate capability. Although the surface area of GSs have been increased with the addition of the nanoparticles, the resulting specific surface area was still much lower than the theoretical surface area of 2630 m²/g of the isolated GSs.

Thus, there is a need for graphene materials having effective surfaces areas approaching the theoretical maximum of 2630 m²/g. Further, there remains a need for a method of reliably producing the same. The present novel technology addresses these needs.

DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic illustration of the graphene sheet (GS) and the graphene sheet nanocarbon composites (GSNC) preparation process.

FIG. 2 graphically illustrates nitrogen adsorption and desorption of the as-prepared GNCs with different nanocarbon content.

FIG. 3A illustrates TEM images of the as-prepared GSNCs from pure GSs.

FIG. 3B illustrates TEM images of the as-prepared GSNCs with 1% nanocarbon content and a surface area of 1256 m²/g.

FIG. 3C illustrates TEM images of the as-prepared GSNCs with functionalized nanocarbons.

FIG. 3D illustrates TEM images of the as-prepared GSNCs with 1% nanocarbon content and a surface area of 1256 m²/g.

FIG. 4A presents SEM images of the pure GSs.

FIG. 4B presents SEM images of GSNCs with a 1% nanocarbon content and a surface area of 1256 m²/g after drying.

FIG. 5A graphically illustrates CV curves of the as-prepared GSNCs with a surface area of 1256 m²/g, measured at potential intervals from -0.2 to 0.8 V (vs. SHE) in 1 M H₂SO₄.

FIG. 5B graphically illustrates the capacitance of the GSNCs with different nanocarbon content as the function of current density.

FIG. 6 schematically illustrates Pt nanoparticle etching process on the surface of graphene sheets, according to another embodiment of the present novel technology.

FIG. 7A is a first atomic resolution electron micrographs showing the dynamic etching of graphene sheets by Pt nanoparticles and the resulting trenches left behind in the graphene according to the embodiment of FIG. 6.

FIG. 7B is a second atomic resolution electron micrographs showing the dynamic etching of graphene sheets by Pt nanoparticles and the resulting trenches left behind in the graphene according to the embodiment of FIG. 7A.

FIG. 7C is a third atomic resolution electron micrographs showing the dynamic etching of graphene sheets by Pt nanoparticles and the resulting trenches left behind in the graphene according to the embodiment of FIG. 7A.

FIG. 7D is a fourth atomic resolution electron micrographs showing the dynamic etching of graphene sheets by Pt nanoparticles and the resulting tortured path left behind in the graphene according to the embodiment of FIG. 6.

FIG. 7E is a fifth atomic resolution electron micrographs showing the dynamic etching of graphene sheets by Pt nanoparticles and the resulting etch path left behind in the graphene according to the embodiment of FIG. 7D.

FIG. 7F is a sixth atomic resolution electron micrographs showing the dynamic etching of graphene sheets by Pt nanoparticles and the resulting etch path left behind in the graphene according to the embodiment of FIG. 7D.

FIG. 8A is an electron micrograph of pristine graphene.

FIG. 8B is an electron micrograph of Pt nanoparticles etched graphene according to the embodiment of FIG. 6.

FIG. 9 graphically illustrates the XPS spectra of graphene before and after Pt nanoparticulate etching, according to the embodiment of FIG. 6.

FIG. 10A graphically illustrates the N_2 adsorption isotherms and CO_2 capture properties of graphene composites for graphene, Pt/Graphene, and Pt/Graphene 800 °C at 77 K. P/P° , relative pressure; STP, standard temperature and pressure.

FIG. 10B graphically illustrates the N_2 adsorption isotherms and CO_2 capture properties of graphene composites for graphene, Pt/Graphene, and Pt/Graphene 800 °C at 273 K; filled and open symbols represent adsorption and desorption branches, respectively.

FIG. 11 is a schematic illustration of a supercapacitor using electrodes made from the embodiment of FIG. 1.

DESCRIPTION OF PREFERRED EMBODIMENTS

For the purposes of promoting an understanding of the principles of the novel technology, reference will now be made to the embodiments illustrated in the drawings and specific language will be used to describe the same. It will nevertheless be understood that no limitation of the scope of the novel technology is thereby intended, such alterations and further modifications in the illustrated device, and such further applications of the principles of the novel technology as illustrated therein being contemplated as would normally occur to one skilled in the art to which the novel technology relates.

According to a first embodiment of the present novel technology, as illustrated in FIGs. 1-5B, graphene sheets 10 were prepared by the exfoliation of graphite oxide (a layered material consisting of hydrophilic oxygenated graphene sheets with oxygen functional groups on their basal planes and edges), such as in water to yield a colloidal suspension of almost entirely individual graphene sheets 10. Nanosized carbon particles 15, typically carbon black particles 15, were functionalized with hydrophilic groups, such as $-\text{SO}_3\text{H}$ (i.e., bisulfate or hydrogen sulfite), and the GSNCs 20 were prepared with different loadings of the functionalized carbon black particles 25 by simultaneous chemical reduction of both the graphene oxides 30 and the functionalized carbon black particles 25 while in solution. Functionalization is the addition of functional groups onto the surface of a material by chemical synthesis methods or the like, and the functional group added can be subjected to ordinary synthesis methods to attach virtually any kind of compound onto

the material's surface. The nanosized functionalized carbon black particles 25 attached to the surface of the GSs 10 and served as spacers to separate/support the neighboring GSs 10, which prevented the haphazard restacking of the graphene sheets 10 into a randomly oriented solid particulate mass, and consequently, resulted in the generation of increased surface area. The specific surface area of the composites 20 was 1256 m²/g, and a maximum specific capacitance of 240 F/g was observed at a current density of 1A/g. In addition, graphene sheet composite-based capacitors using this composite material 20 for the electrodes exhibited enhanced rate capability, the maximum sustainable continuous or pulsed current output. The above improved electrochemical performance of the GSNCs 20 is a product of their high surface area and high electronic conductivity of the GSs 10.

While the carbon nanoparticles 15 discussed herein are specifically carbon black, other allotropes of carbon may be selected. Amorphous carbon, glass carbon, coke, carbon graphitized to various degrees of graphitization, diamondlike carbon, and diamond may also be selected, with the electrical and physical properties of the resulting composite material 20 varying as a result.

In the synthesis of the GSNCs 20, the GSs 10 were obtained by *in situ* chemical reduction of exfoliated graphene oxides 30. As shown in FIG. 1, the construction of the GSNCs involved the following steps: first, exfoliation 40 of graphite oxides, then, mixing 45 the graphene oxide sheets 30 and functionalized nanocarbons 25, and finally, chemical reduction 50 of the mixture. The nanocarbons 15 were functionalized 55 by the dizonium reaction, and the nanocarbons 25 are highly hydrophilic after functionalization 55. Graphene oxide sheets 30 exist in the

liquid dispersion 60. After reduction 50 of the compound 20 in its solid state, the graphene sheets 10 aggregate 65 and stack back into a layer structure like graphite. Graphene oxide sheets 30 and carbon nanoparticles 25 exist together in dispersion 60; in the solid state the nanocarbons 25 serve as spacers, preventing the graphene sheets 10 from restacking back to the graphite structure, and thus make the graphene sheet 10 accessible on both sides and allowing access to the high surface area graphene composite 20. In the reduction process 50, the well-dispersed graphene oxide sheets 30 and the functionalized nanocarbons 25 were reduced simultaneously and the functionalized nanocarbon particles 25 became anchored 75 to the graphene sheets 10. The solid composites 20 float on the surface of the transparent liquid phase of the dispersion 60. The resultant graphene sheets 10 with attached functionalized nanocarbons 25 aggregated together to yield the GSNCs 20 upon drying.

Graphene oxides 30, possessing a considerable amount of hydroxyl and epoxide functional groups on both surfaces of each sheet 30, and carboxyl groups, mostly at the sheet edges, are strongly hydrophilic and can easily disperse in water. The nanocarbons 15 were functionalized 55 by diazonium reactions as shown in FIG. 1A. In this process, the hydrophilic $-SO_3H$ functional group was grafted onto the surface of the nanocarbons 15. As shown in FIG. 1, after functionalization 55 the nanocarbons 25 can disperse well in the water even if left for several months. After adding the functionalized nanocarbons 25 into the graphene sheet dispersion 60, the two materials were able to be easily mixed and formed uniform dispersion 60.

In order to explore the effects of the nanocarbon content on the composite surface areas, a series of controlled experiments were conducted by varying the content of the nanocarbon in the GSNCs 20 to 0, 0.5, 0.8 and 1 wt.%. The addition of the nanocarbons 25 into the dispersion 60 of the graphene sheets 30 led to the formation of well-dispersed nanocarbon particles 25 on the surface of the graphene sheets 30. The *in situ* formed nanocarbon particles 25 can serve as spacers to prevent aggregation/restacking of the individual graphene sheets 30 in the dispersion during the drying process and form a particle-sheet structured GSNC 20 in the solid state. It is reasonably expected that the *in-situ*-formed composites 20 have more of a rich porous structure and large available surface area for the charge-storage process than those obtained by drying the pure graphene sheets 10, in which the restacking of the graphene sheets 10 inevitably occurs.

The nitrogen-adsorption and -desorption isotherms of the as-prepared GSs 10 with different nanocarbon content exhibited type IV characteristics (FIG. 2), which are indicative of the presence of relatively large pores in the composites 20. It is worth noting that the Brunauer-Emmett-Teller (BET) specific surface area of the graphene sheets without the addition of nanocarbons (77 m²/g) was much lower than the theoretical predictions for the isolated graphene sheets (2630 m²/g). With the increase in nanocarbon content in the composites 20, the specific surface area also increased. The BET-specific surface area of the composites 20 with nanocarbon content of 1wt.% reached as high as 1256 m²/g, which is much higher than that of the nanocarbons 25 (790 m²/g) and the pure GS 10 (77 m²/g). In further trials, the BET-specific surface area of the composites 20 with additional nanocarbon material

25 was observed to be up to 1875 m²/g, and values as high as 2000, 2100 and approaching the theoretical maximum are expected.

The large specific surface area suggests that the introduction of nanocarbon particles 25 between 2D graphene sheets 10 effectively limits the face-to-face stacking from about forty layers of graphene sheets 10 per stack to about two layers of graphene sheets 10 per stack when compared with that of dried pure GS 80.

To further characterize the structure of the GSNCs 20, the samples were examined using transmission electron microscopy (TEM) and scanning electron microscopy (SEM) (FIGs. 3 and 4). For comparison, the TEM images of the reduced GSs 10 without nanocarbons 15 and the functionalized nanocarbons 25 (FIG. 3A and 3D) are also presented. FIG. 3A shows that the pure GSs 80 prepared by chemical reduction 50 were transparent with some wrinkles visible under TEM. The morphology of functionalized nanocarbons 25 can be seen in Figure 3B, which shows that the functionalized nanocarbon particles 25 were in the range of 5-30 nm, and that they tended to spontaneously agglomerate together to form large particles. The structure of the GSNCs 20 is shown in FIG. 3C, which clearly shows that the functionalized nanocarbons 25 were homogeneously anchored 75 onto the surface of the graphene sheets 30 (FIGs. 3C and 3D). Through further comparisons of FIGs. 3A & 3B with FIGs. 3C & 3D, it is clear that the graphene sheets 30 served as substrates to anchor 75 the hydrophilic nanocarbon particles 25. Without the addition of the nanocarbons, it can be seen that the pure GS 80 was less transparent than the as-prepared GSNCs 20, because the pure graphene sheet 10 spontaneously agglomerated/restacked back and formed a thick graphene sheet stack 80 (which

has many more layers of graphene sheet than that of the GSNC 20) after drying. The GSs 10 in the composites 20 were almost transparent, which suggests that the GSs 10 were well separated by the nanocarbon particles 25. The number of layers of graphene sheets 10 in the composites 20 was lower (typically about two layers of GS 10, as suggested by BET data). Considering that sonication was used during the preparation of TEM specimens, the above observation also demonstrates the strong interactions/bonding between the nanocarbon carbon particles 25 and the graphene sheet 10 surface. The SEM images also clearly show the difference between the pure GS agglomerations 80 and the GSNCs 20. The pure GSs 10 after drying tended to restack and form solid particles 80 (FIG. 4A). However, the layered structure can be seen clearly for GSNCs 20, as the small nanocarbon particles 25 are highly dispersed on the graphene sheet 10 surfaces and served as spacers to prevent the graphene sheets 10 from restacking, which is consistent with the observed increased surface area of the graphene sheet/nanocarbon composites 20.

Recently, GS agglomerates 80 have been used as electrodes for supercapacitors; for example, chemically modified GSs electrode active materials in supercapacitors have been found to exhibit a specific capacitance of 135 F/g and 99F/g in aqueous KOH and organic electrolytes, respectively. GS specimens 80 having a measured surface area of 534 m²/g have exhibited a capacitance of 150 F/g under the specific current 0.1 A/g. Based on the structure of the GSNCs material 20, the composite 20 likewise is expected to have good electron conductivity, low diffusion resistance to protons/cations, easy electrolyte penetration, and high electroactive areas. Such composites 20 are promising candidates for electrode

active materials for supercapacitors 100, yielding high performance energy storage devices.

The properties of these GSNCs 20 were measured using cyclic voltammetry (CV) and galvanostatic charge/discharge. The galvanostatic charge/discharge was used to calculate the specific capacitance of the GSNCs 20. The CV curves (FIG. 5A) were nearly rectangular in shape, indicating a good charge propagation within the electrode. For the supercapacitor 100 using the activated carbon-based electrodes 105, the CV curve shape and the specific capacitance significantly degraded as the voltage scan rate increased. In contrast, as the scan rate increased, the GSNCs 100 base electrode 105 remained a rectangular shape with little variance, even at a scan rate of 200 mV/s (FIG. 5). Another indication of good charge propagation is the low variation of specific capacitance with the increase of the charge/discharge current density as shown in Figures 5B and 5C. The capacitance of the GSNCs 20 was 256 F/g at a discharge current density of 1A/g, and the capacitance was 218 F/g when the discharge current density increased to 5A/g, leaving only a 14.8% loss with the 400% increase on the discharge current density. Therefore, the added nanocarbons played a very important role in the electrochemical performance of the composites. The high performance of the GSNC electrode materials 105 in the supercapacitor 100 from the high surface area of this composite 20 is quite beneficial.

The specific capacitance of the GSNCs 20 with different amounts of nanocarbons 25 at various current densities is shown in Figure 5C for comparison. It is worth noting that the specific capacitance of the high surface area GS composites 20 was much higher than that of the pure GSs 80, and the capacitance

increased with the increase of the surface area. Hence, the increased surface area was responsible for the increase of the capacitance. The incorporation of nanocarbon particles 25 into the GSs 20 not only increased the surface area, but also acted as spacers between the graphene sheets 10 to create diffusion paths for the liquid electrolytes, which facilitated the rapid transport of the electrolyte ions, consequently resulting in the improved electrochemical properties of the GSNCs. Therefore, GSNCs 20 with a surface area of 1256 m²/g exhibited the maximum capacitance of 218 F/g at a current density of 5 A/g compared with pure graphene materials 80 with a capacitance of 46 F/g at the same current density, indicating that the unique structure of the novel GSNCs 20 facilitated the rapid transport of the electrolyte ions and electrons throughout the electrode 105.

The simple process for preparing high surface area GSs 20 by simultaneously reducing the graphene oxide sheets 30 and the functionalized nanocarbons 25 is more particularly described below. This method is easily scaled up for the mass-production of high surface area graphenes 20. The nanocarbon particles 25 are generally dispersed uniformly on the surface of the graphene sheets 10, serving as spacers between graphene sheets 10, and preventing the restacking of the GSs 10 after drying or removal of the solvent. Consequently, the GSNC surface area has been observed as high as 1875 m²/g. The unique structure of the GSNCs 20 facilitated the high-rate transportation of electrolyte ions and electrons throughout the electrode 105, resulting in the excellent electrochemical properties. The supercapacitor 100 based on the GSNCs 20 exhibited a specific capacitance of nearly 400 F/g at a current density of 1 A/g in a 1 M H₂SO₄ solution. The specific capacitance

increased with the increase of the composite surface areas. The new high surface area GS material 20 is also useful as a sorbent for hydrogen storage, as a catalyst support for fuel cells, and as a component for other clean energy devices.

Example 1

Synthesis of the graphene oxides (GO) and the functionalized

nanocarbons GO 30 was synthesized from natural graphite powder (325 mesh) by the modified Hummer method. The GO 30 was then suspended 110 in water to yield an opaque dispersion 60, which was subjected to separation by centrifuge (five times) to completely remove residual salts and acids. The purified GO 30 was then dispersed 120 in purified water (0.5 mg/mL). Exfoliation 40 of the GO 30 was achieved by ultrasonication of the dispersion 60 using an ultrasonic bath. During the composite preparation process, the number of single layers in the GSs 30 as a precursor are typically controlled to be as small as possible. Graphite oxide is a layered material consisting of hydrophilic oxygenated GSs (graphene oxides) 30 bearing oxygen functional groups in their basal planes and edges. Under appropriate conditions, graphite oxides can undergo complete exfoliation in water, yielding colloidal suspensions 60 wherein the suspended material is composed almost entirely of individual graphene oxide sheets 30.

For the preparation of the nanosized carbon particles 25, the EC300 carbon blacks 15 were modified with an $-SO_3H$ grafted layer in an aqueous medium by spontaneous reduction 50 of the corresponding *in situ* generated diazonium cation. The modification of EC300 carbon blacks 15 was prepared with a large excess of *in*

situ-generated diazonium cations. In this experiment, 2 g of EC300 carbon blacks 15 were placed in a 0.5 M HCl solution 125 containing 3.5 g of sulfonic acid. The solution 125 was vigorously stirred for thirty minutes before sodium nitrite was added. Next, 3.6 g NaNO_2 was added to the solution 125 in order to ensure a total transformation of the amine into diazonium in spite of the nitrogen oxide gas release. For the reaction to be finished completely, the mixture was stirred for four hours and then heated up to 70 °C for another three hours. Finally, the mixture was filtrated, washed with water, and re-filtrated three times.

Synthesis of the GSNCs GSNCs 20 with different nanocarbon content were prepared by simultaneously reducing 50 the mixture of the graphene oxide sheets 30 and the highly hydrophilic nanocarbons 25. Graphene oxide sheets 30 dispersed in water were mixed with the nanocarbons 25. The mixture was stirred for thirty minutes and then subjected to ultrasonication for one hour at room temperature. Subsequently, a hydrazine solution was added into the mixture and the mixture was stirred and heat treated at 100 °C for 24 hours. Then the mixture was filtered and washed with purified water several times and dried at 60 °C for 24 hours in a vacuum.

Characterization of the composites the morphology of the graphene sheets 10, the nanocarbons 25, and the GSNCs 20 were characterized by a transmission electron microscope. The morphology of the composites 20 was also examined by a scanning electron microscope. The specific surface areas of the graphene sheet 10, the nanocarbons 25, and the GSNCs 20 were measured by the Brunauer-Emmett-Teller (BET) method of nitrogen sorption at the liquid nitrogen

temperature (77 K). Further, the composite materials 20 are stable at elevated temperatures and exhibit degradation or etching at the nanocarbon particle 25 sites.

Preparation and characterization of the supercapacitor electrode: A three-electrode-cell system was used to evaluate electrochemical performance using both cyclic voltammetry and galvanostatic charge/discharge techniques using an electrochemical workstation. A 1M H₂SO₄ aqueous solution was used as the electrolyte. A platinum sheet and a saturated Ag/AgCl electrode were used as the counter and the reference electrodes, respectively. The working electrode 105 was prepared by casting a Nafion-impregnated sample onto a glassy carbon electrode with a diameter of 5 mm. Next, 17.5 mg of composite material 20 was dispersed by sonication for ten minutes in a 10 mL water solution containing 5 μ L of a Nafion solution (5 wt.% in water). This sample (10 μ L) was then dropped onto the glassy carbon electrode and dried overnight before electrochemical testing. The specific gravimetric capacitance was obtained from the discharge process according to the following equation:

$$C = \frac{I\Delta t}{\Delta V m}$$

where I is the current load (A), Δt is the discharge time (s), ΔV is the potential change during the discharge process, and m is the mass of active material in a single electrode (g).

Graphene 10 is generally quite inert when exposed to gases such as oxygen and hydrogen at room temperature. At high temperatures, oxygen exposure can

cause preferential etching at defects and edges because the carbon atoms at the defects and edges are extremely reactive (this is because the p_z electrons of these carbon atoms may not be involved in the conjugated electron system). In a hydrogen atmosphere, the carbon atoms in the graphene bulk remain inert even at high temperatures. However, carbon atoms both at defects and at the edges of a graphene sheet become very active when a reactive metal is positioned proximate to these atoms. At high temperatures, Pt nanoparticles 150 may be used to etch graphene 10 through the catalytic hydrogenation of carbon, where carbon atoms on the graphene edges dissociate on the surface of Pt nanoparticle 150 and then react with H_2 at the Pt nanoparticle 150 surface to form methane. This process is shown schematically in Fig. 6. In contrast, such etching does not occur on graphene materials at carbon black or like carbonaceous particle sites.

The mechanism of etching of graphene 10 by Pt nanoparticles 150 at elevated temperature was observed *in-situ* using high-resolution environmental transmission electron microscopy. Graphene sheets 10 were loaded with 20 weight percent of Pt nanoparticles 150, and subsequently placed onto a lacey carbon TEM grid. The Pt nanoparticles 150 are typically sized between a few nanometers up to ten microns across, and may even be larger. More typically, the Pt nanoparticles are between about 5 and about 80 nanometers in diameter, although the Pt nanoparticles 150 may more typically range from about 10 nanometers to about 50 nanometers in diameter. The Pt nanoparticles 150 are typically generally spherical, but may exhibit other morphologies. Further, the nanoparticles 150 may be made of PT-like materials, such as PT, Pd, Ni, combinations thereof, and the like. Likewise, in this example, the

graphene sheets 10 were loaded with 20 weight percent Pt nanoparticles 150, but the nanoparticle loading may typically vary from less than about 1 weight percent to as much as 50 weight percent, or more. The graphene samples 10 were heated to 800 °C and hydrogen gas was slowly introduced into the TEM objective lens, and equilibrated at a pressure of approximately 50 mTorr. As the graphene 10 began to etch adjacent the Pt nanoparticles 150, the process was imaged continuously through the use of a high-frame rate camera. Image sequences extracted therefrom are presented as Figure 7A-7F. Initially, the Pt nanoparticles 150 were static after the hydrogen gas was introduced. Eventually, as shown in FIGs. 7A-7C, the Pt nanoparticles 150 began to react with the graphene 10 at defect sites and the hydrogen gas to produce methane. Only those carbon atoms making up the graphene sheet 10 that were in direct contact with these Pt nanoparticles 150 were able to participate in this Pt-catalyzed hydrogenation reaction 155. Once the process was initiated, the conversion process was able to continue, as there are an abundance of defects sites created continuously following the onset of the etching process 155, leading to a self-sustaining reaction. In this case a straight trench was etched through the graphene sheet 10 (Fig. 7C). In other cases, the etching process 155 did not follow a straight line, but rather followed a more tortuous pathway (FIGs. 7D-7F). During the graphene etching process 155, the Pt nanoparticles 150 were observed to maintain a crystallographic relationship with the graphene sheet 10. After etching 155, the Pt nanoparticles 150 are typically reclaimed and saved for future use. These observations indicate that the interaction between the Pt 150 and the graphene 10 at elevated temperature can create a variety of in-plane nanostructures 160 in the

graphene 10. The result of these interactions is the formation of nanoscale trenches, ribbons and islands 160 – and thus a dense network of edge sites 165.

Typically, the graphene sheets 10 are heated to a temperature sufficient for the etching process 155 to occur at a desired rate. The graphene sheets 10 carrying dispersed Pt nanoparticles 150 are typically heated to at least about 700 degrees Celsius, and are more typically heated to a temperature in the range from 750 degrees Celsius to 900 degrees Celsius. Likewise, a hydrogen gas environment supports the Pt-catalyzed hydrogenation reaction 155, although other reducing environments may also be selected.

In graphene 10, each carbon atom uses 3 of its 4 valance band ($2s$, $2p$) electrons (which occupy the sp^2 orbits) to form covalent bonds with the neighboring carbon atoms in the same plane. Each carbon atom in the graphene 10 contributes its fourth lone electron (occupying the p_z orbit) to form a delocalized electron system. Thus, the carbon atoms in the graphene plane 10 (excluding the carbon atoms on the defect sites such as the edges and holes) are saturated carbon atoms, with the three sp^2 electrons forming three covalent bonds and the fourth p_z electron forming a π bond. Real time observations indicate that the heat treatment process creates an abundance of defective edges 165, in the form of embedded nanostructures of trenches, ribbons and islands 160 in the multilayer graphene sheets 10 (see FIGs. 7 and 8B). The resulting materials are anisotropic, having different properties in-plane and out-plane. Importantly, the carbon atoms along the edges of the resulting trenches, ribbons, and the islands 160 are likely to be unsaturated, with one of the electrons in the sp^2 orbitals not forming a covalent

bond with the other carbon atoms. These unsaturated carbon atoms were observed not only from the nano-scale *in situ* TEM images/video (FIG.7), but also from the macro-scale XPS results in Fig.9, which shows an 42.4% increase of the shake-up peak for the graphene sheet 10 after etching 155 (the shake-up peaks correspond to the unsaturated carbon atoms/dangling carbons).

The resulting material provides an important platform for a wide variety of applications, including in catalysis, biomedical science, polymer science and energy science. This is because these unsaturated carbon atoms allow graphene 10 to be functionalized by chemically grafting other compounds or groups thereonto. Thus, these functionalized graphene 170 can be used, for example, sensors, catalysts, sorbents, and the like. Without such features, it is difficult to chemically graft compounds or groups onto graphene 10. These unsaturated carbons also promote the establishment of weak bonding between graphene and other species. One such application is gas physisorption. Of particular interest is the physisorption of carbon dioxide. The p_z electrons and one sp^2 electron of these unsaturated carbon atoms at the defects sites will be available for bonding and will more readily form bonds with CO₂ molecules, which could in turn result in a significant improvement in CO₂ adsorption. The adsorbed CO₂ molecules (or other gas molecules) may be stored for later removal or reaction.

While the novel technology has been illustrated and described in detail in the drawings and foregoing description, the same is to be considered as illustrative and not restrictive in character. It is understood that the embodiments have been

shown and described in the foregoing specification in satisfaction of the best mode and enablement requirements. It is understood that one of ordinary skill in the art could readily make a nigh-infinite number of insubstantial changes and modifications to the above-described embodiments and that it would be impractical to attempt to describe all such embodiment variations in the present specification. Accordingly, it is understood that all changes and modifications that come within the spirit of the novel technology are desired to be protected.

Claims

We claim:

1. A carbon composite material, comprising:
a plurality of spaced graphene sheets, each respective sheet having opposed generally planar surfaces; and
a plurality of functionalized carbonaceous particles;
wherein at least some functionalized carbonaceous particles are disposed between any two adjacent graphene sheets;
wherein each respective at least some functionalized carbonaceous particle is attached to both respective any two adjacent graphene sheets;
wherein each respective graphene sheet comprises at least one layer of graphene; and
wherein at least portions of respective any two adjacent graphene sheets are oriented substantially parallel with one another.
2. The composite material of claim 1 wherein the carbonaceous particles are substantially amorphous carbon.
3. The composite material of claim 2 wherein the carbonaceous particles are functionalized with $\text{-SO}_3\text{H}$ radicals.
4. The composite material of claim 1 wherein the carbonaceous particles are generally spherical.

5. The composite material of claim 4 wherein the carbonaceous particles are between about 5 nm and about 80 nm in diameter.
6. The composite material of claim 1 wherein the plurality of graphene sheets includes at least three graphene sheets.
7. The composite material of claim 1 wherein the composite material has a specific surface area of at least about 800 m²/gm.
8. The composite material of claim 1 wherein the composite material has a specific surface area of at least about 1200 m²/gm.
9. The composite material of claim 1 wherein the composite material has a specific surface area of at least about 1800 m²/gm.
10. The composite material of claim 1 wherein the carbonaceous particles account for about 1 weight percent of the composite material.

11. A method of manufacturing a high surface area graphene composite material, comprising:

a) substantially removing residual salts and acids from graphite oxide to yield purified graphite oxide;

b) exfoliating the purified graphite oxide to yield graphite oxide sheets;

c) functionalizing carbonaceous particles with hydrophilic radicals;

d) infiltrating graphite oxide sheets with functionalized carbonaceous particles;

e) anchoring functionalized carbonaceous particles onto graphite oxide sheets to yield particle-treated graphite oxide sheets; and

f) reducing particle-treated graphite oxide sheets to yield graphene sheets.

12. The method of claim 11 and further comprising:

g) drying graphene sheets;

h) stacking dried graphene sheets to yield a solid composite graphene material.

13. The method of claim 11 wherein the carbonaceous particles are generally spherical amorphous carbon particles between about 5 nm and about 80 nm in diameter.

14. The method of claim 11 wherein the carbonaceous particle treated graphene sheets have a specific surface area of at least about 800 m²/gm.
15. The method of claim 11 wherein the carbonaceous particle treated graphene sheets have a specific surface area of at least about 1200 m²/gm.
16. The method of claim 11 wherein the carbonaceous particle treated graphene sheets have a specific surface area of at least about 1800 m²/gm.
17. An energy storage device, comprising:
an energy storage portion; and
two electrodes, each respective electrode operationally connected to the energy storage portion;
wherein at least one electrode further comprises:
a plurality of stacked generally parallel graphene layers; and
a plurality of functionalized carbon particles disposed between respective adjacent graphene layers for propping respective adjacent graphene layers apart.
18. The energy storage device of claim 17 wherein the functionalized carbon particles are generally spherical amorphous carbon particles sized between about 5 nm and about 80 nm in diameter.

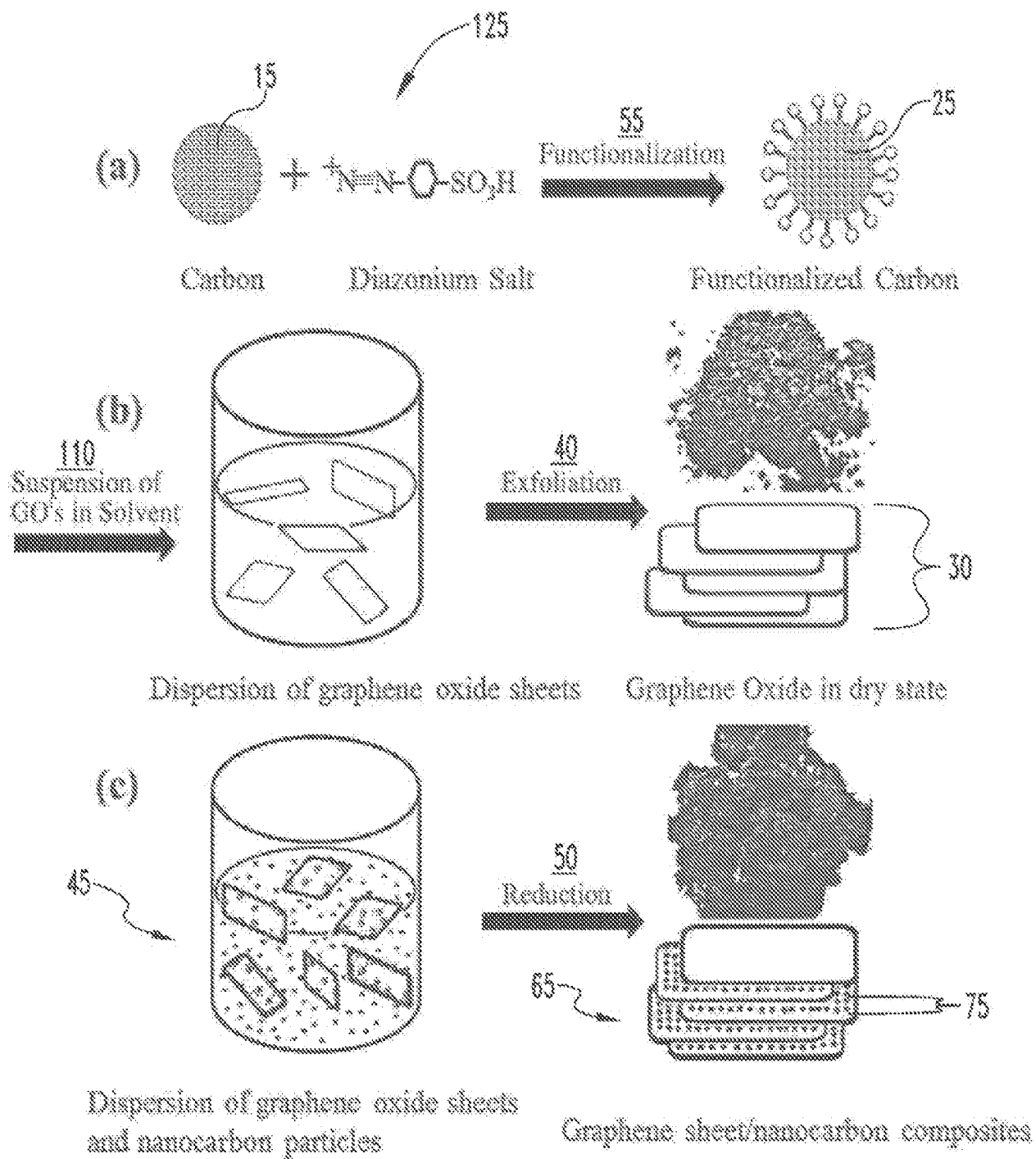
19. The energy storage device of claim 17 wherein the at least one electrode has a specific surface area of at least about 1800 m²/gm.

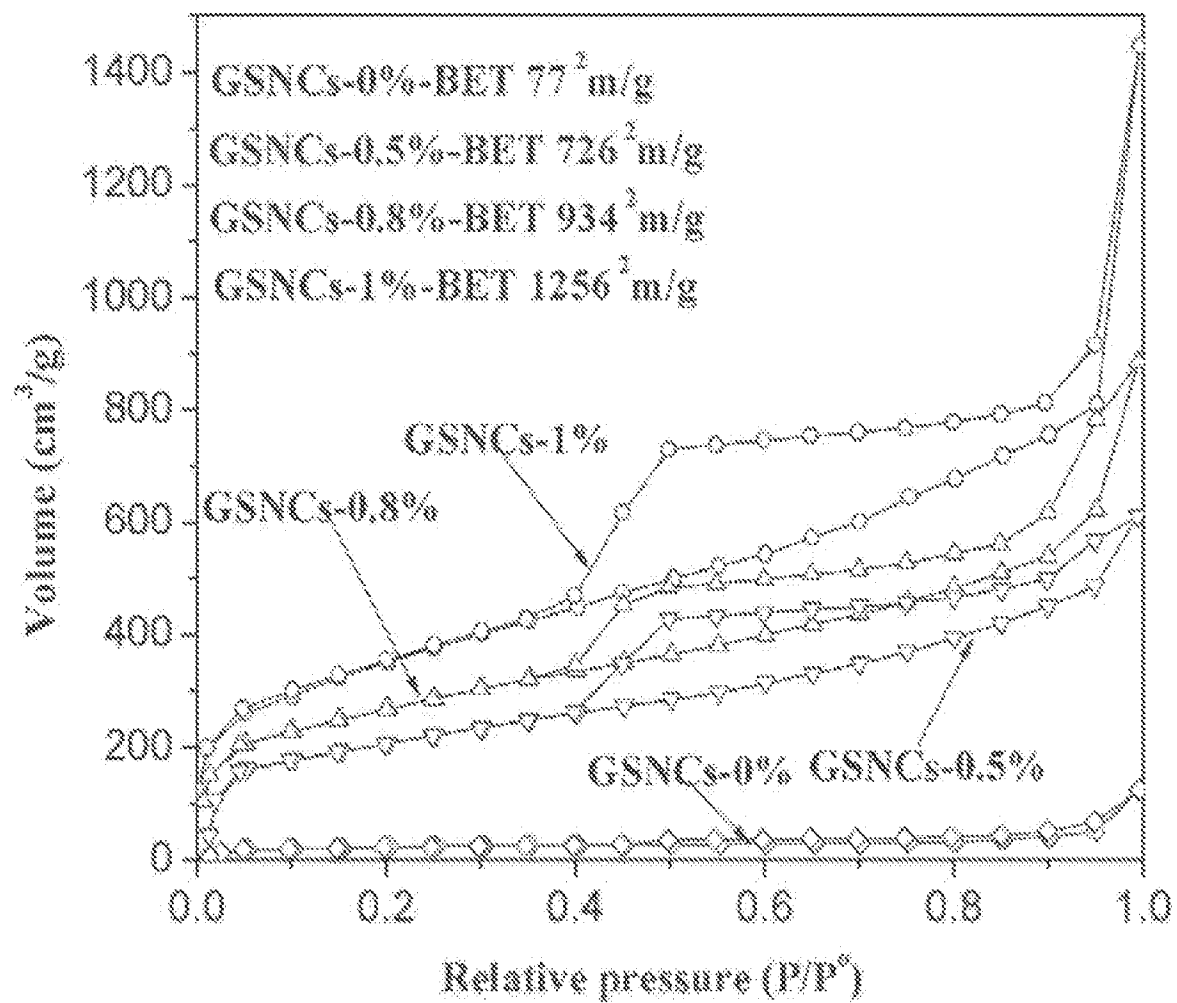
20. The energy storage device of claim 19 wherein the capacitance of the at least one electrode is about 250 F/gm at a discharge current density of about 1A/gm and wherein the capacitance of the at least one electrode is about 220 F/gm at a discharge current density of about 5A/gm.

21. An energy storage apparatus, comprising:
an electrochemical cell;
two electrodes, each respective electrode operationally connected to opposite poles of the electrochemical cell;
wherein ions undergo a redox reaction at the surface of at least one electrode;
wherein the at least one electrode further comprises:
a plurality of stacked graphene layers; and
a plurality of functionalized carbon particles disposed between respective adjacent graphene layers for propping the respective adjacent graphene layers apart.

22. A method of etching graphene, comprising:
- identifying a graphene surface to be etched;
 - positioning platinum particles on the graphene surface;
 - elevating the temperature of the graphene surface to about 800 degrees Celsius;
 - placing the graphene surface into a hydrogen gas environment;
 - initiating removal of carbon atoms from the graphene surface through hydrogenation at defect sites adjacent Pt nanoparticles; and
 - etching embedded nanostructures into the graphene surface.
23. The method of claim 22 wherein the identified graphene surface is part of a multilayered graphene structure defining a plurality of graphene layers separated by carbon particles positioned between respective graphene layers.
24. A method for storing gas, comprising:
- identifying a multilayer graphene structure defining a plurality of graphene layers separated by carbon particles positioned between respective graphene layers, wherein the multilayer graphene structure has a specific surface area of at least about 1200 m²/gm; and
 - adsorbing gas onto the multilayer graphene structure.
25. The method of claim 24 and further comprising:
- removing adsorbed gas from the multilayer graphene structure.

26. The method of claim 24 and further comprising:
reacting adsorbed gas on the multilayer graphene structure.

**Fig. 1**

**Fig. 2**

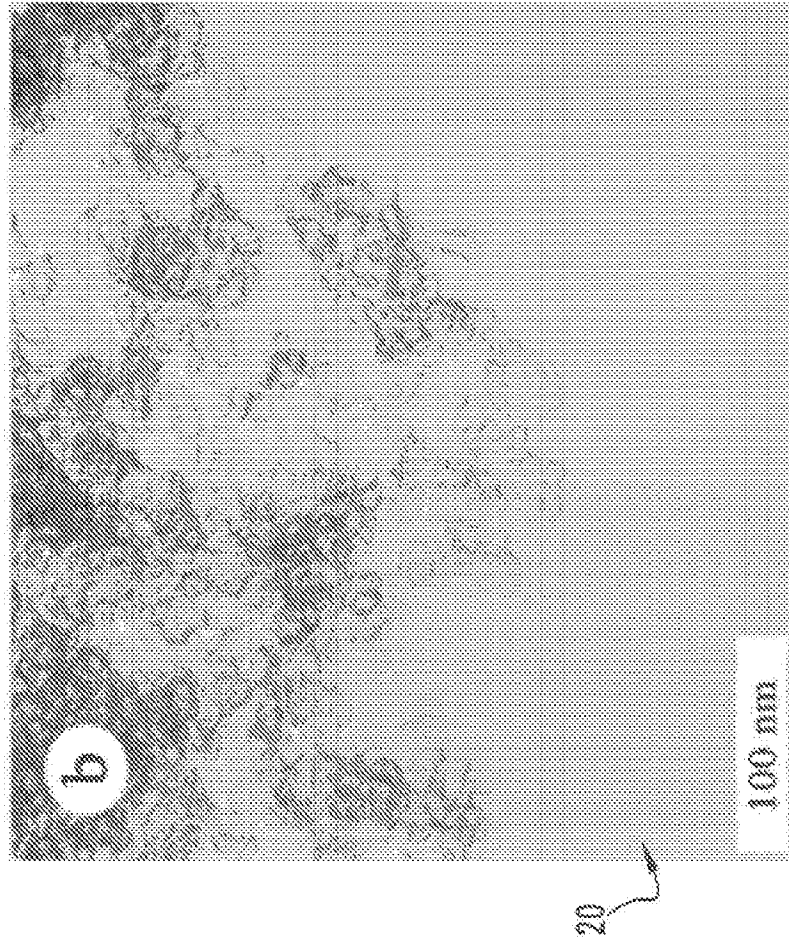


Fig. 3B



Fig. 3A

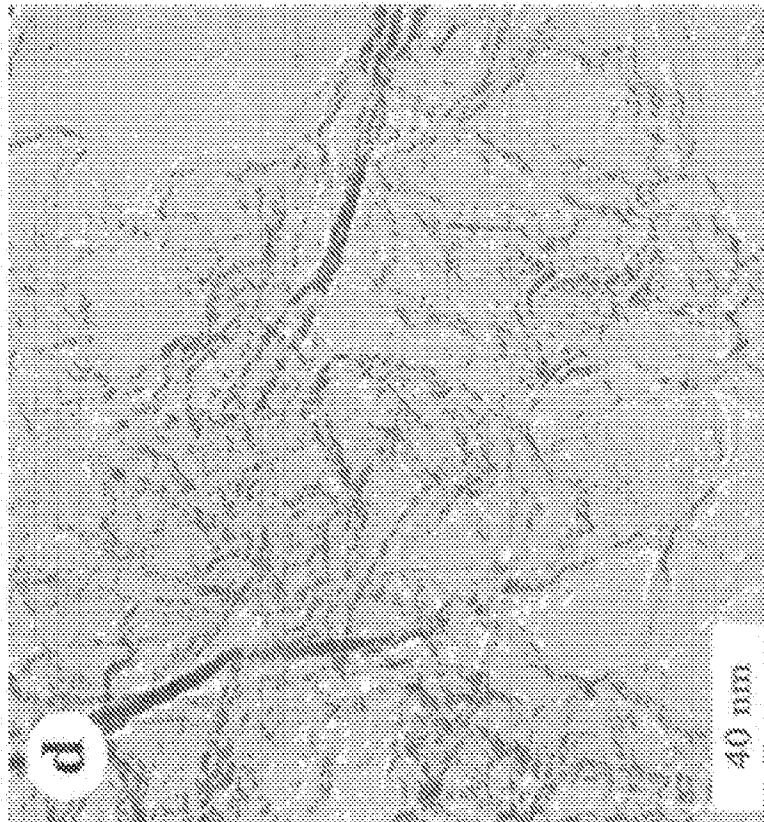


Fig. 3D

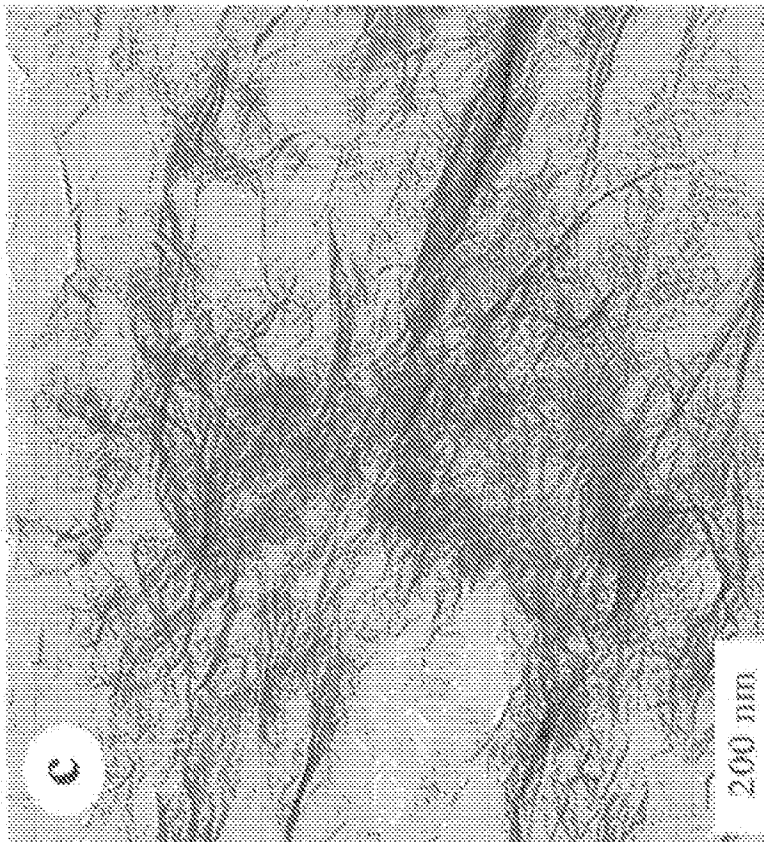
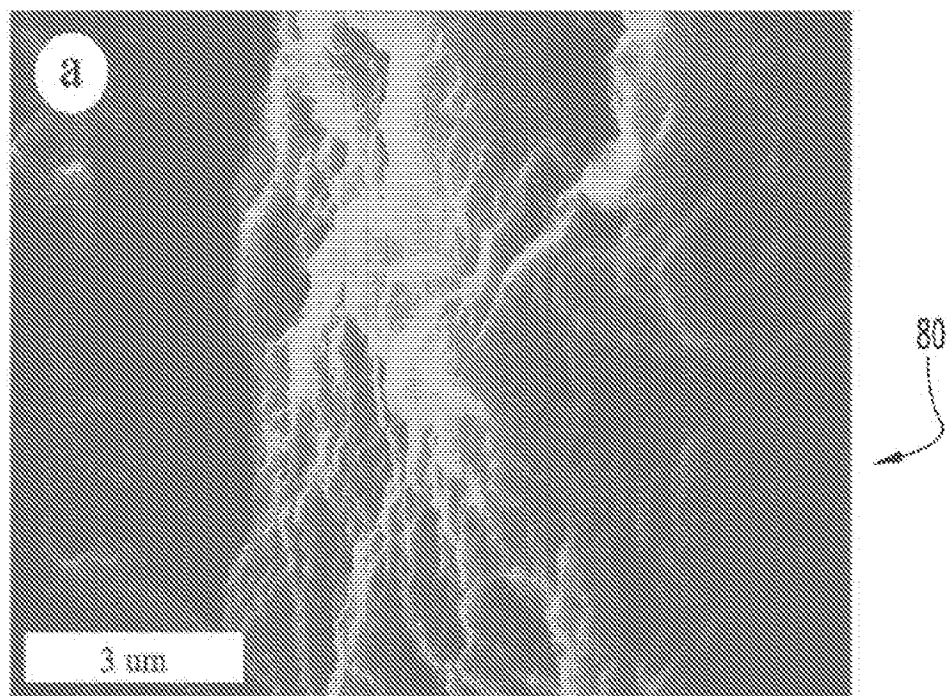
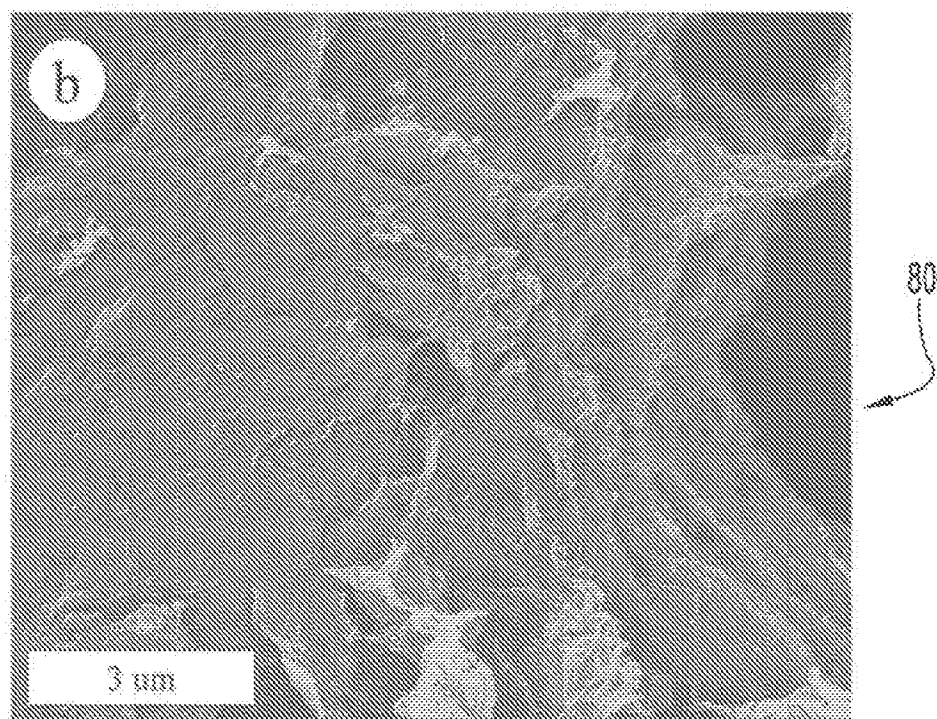
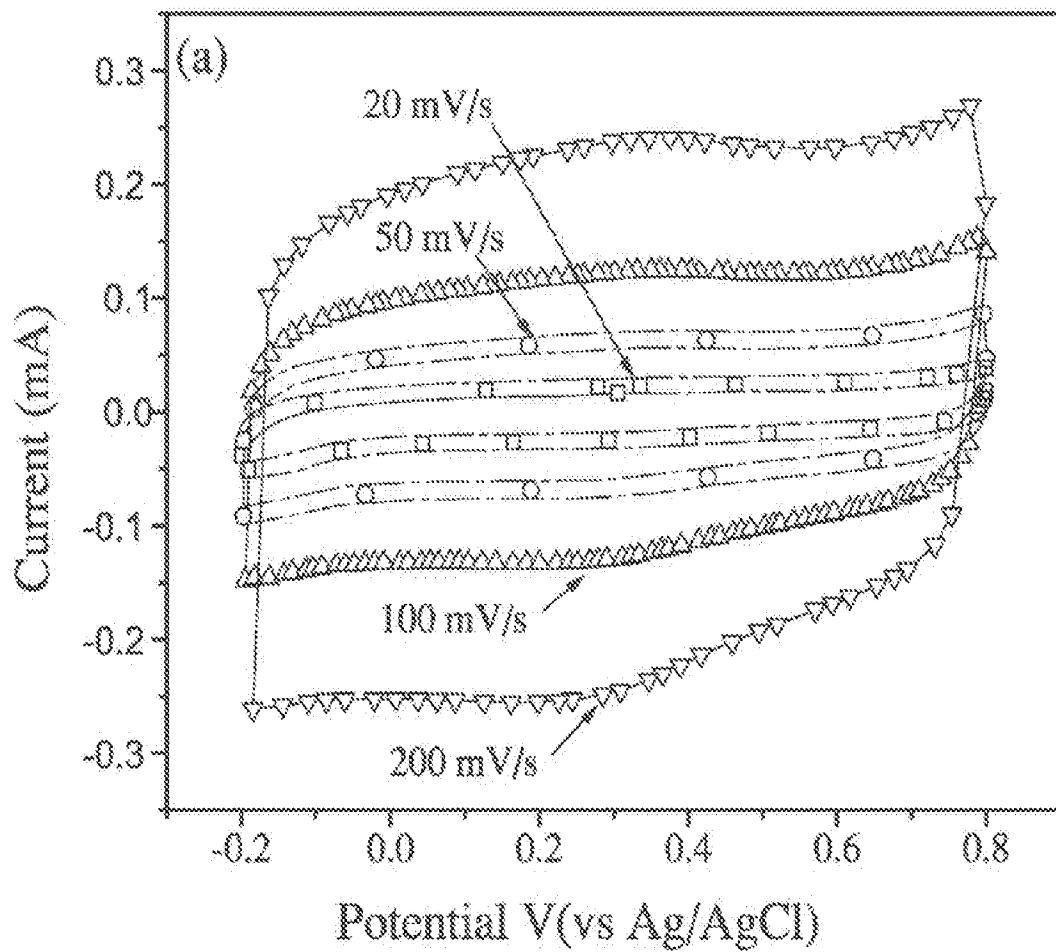
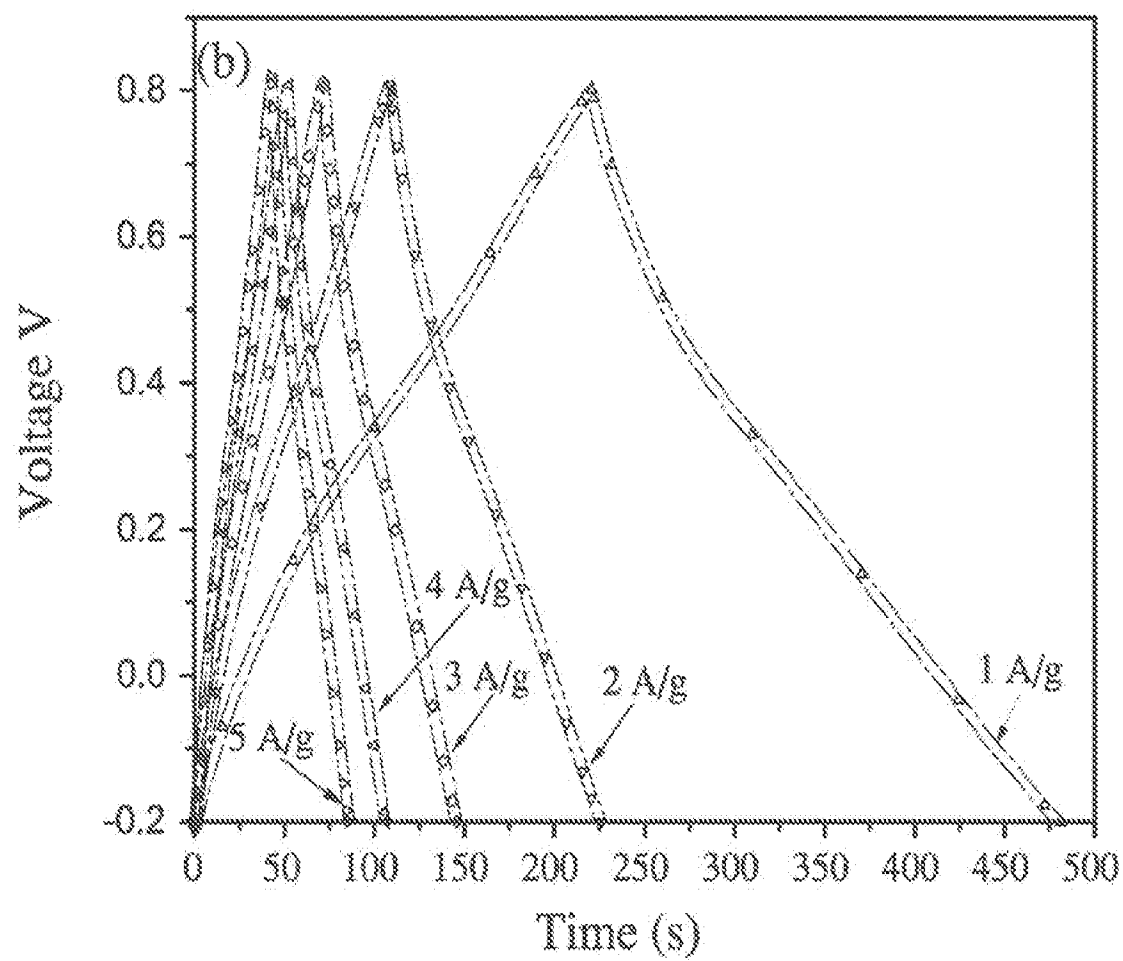
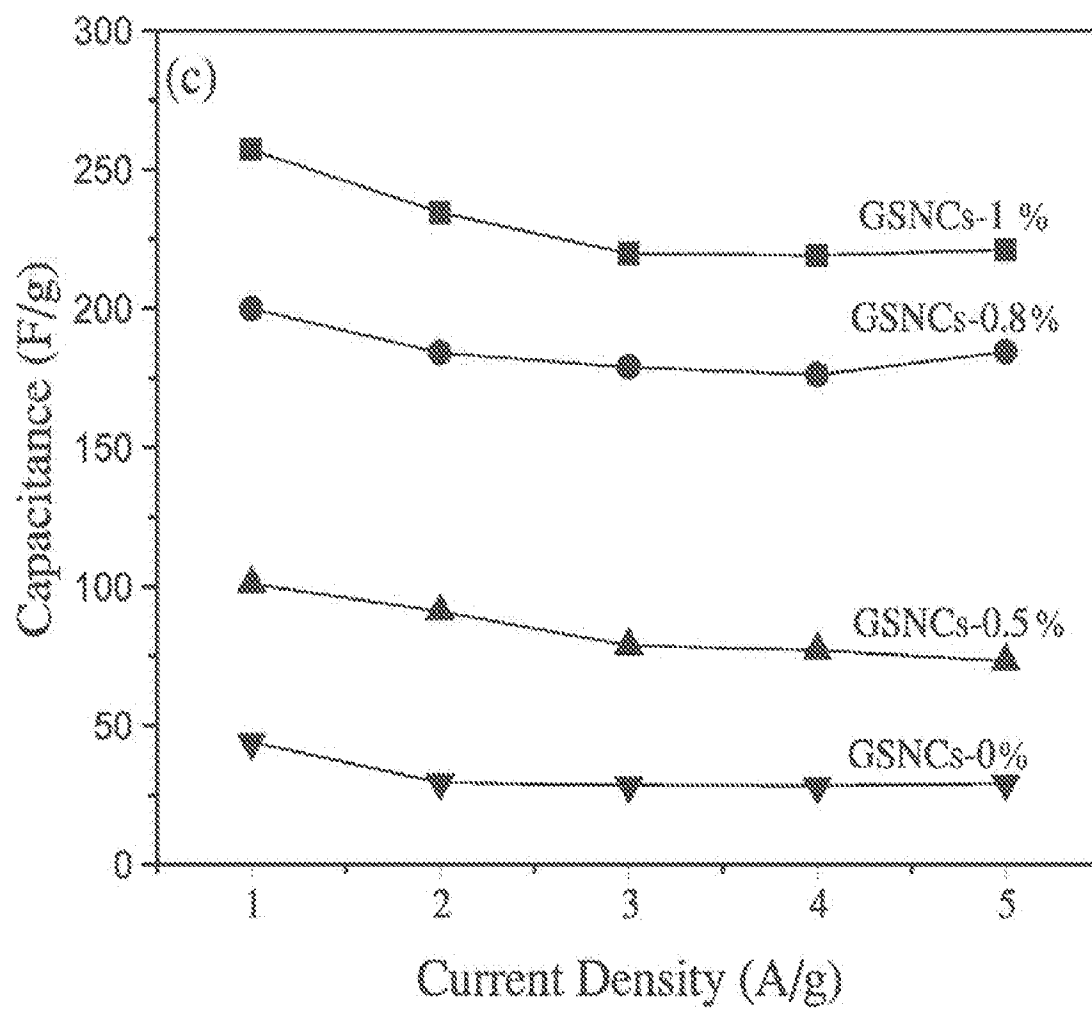


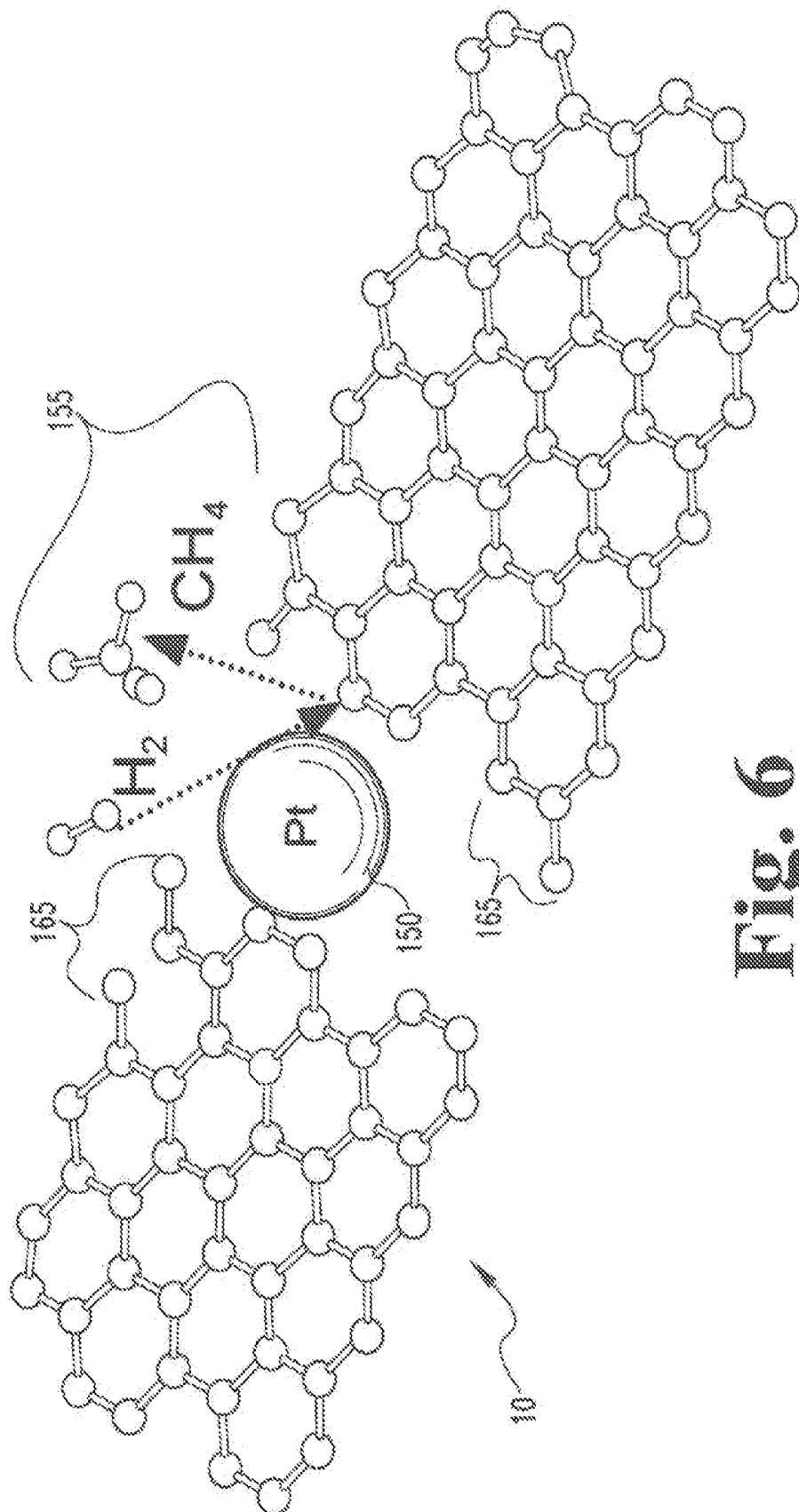
Fig. 3C

**Fig. 4A****Fig. 4B**

**Fig. 5A**

**Fig. 5B**

**Fig. 5C**

**Fig. 6**

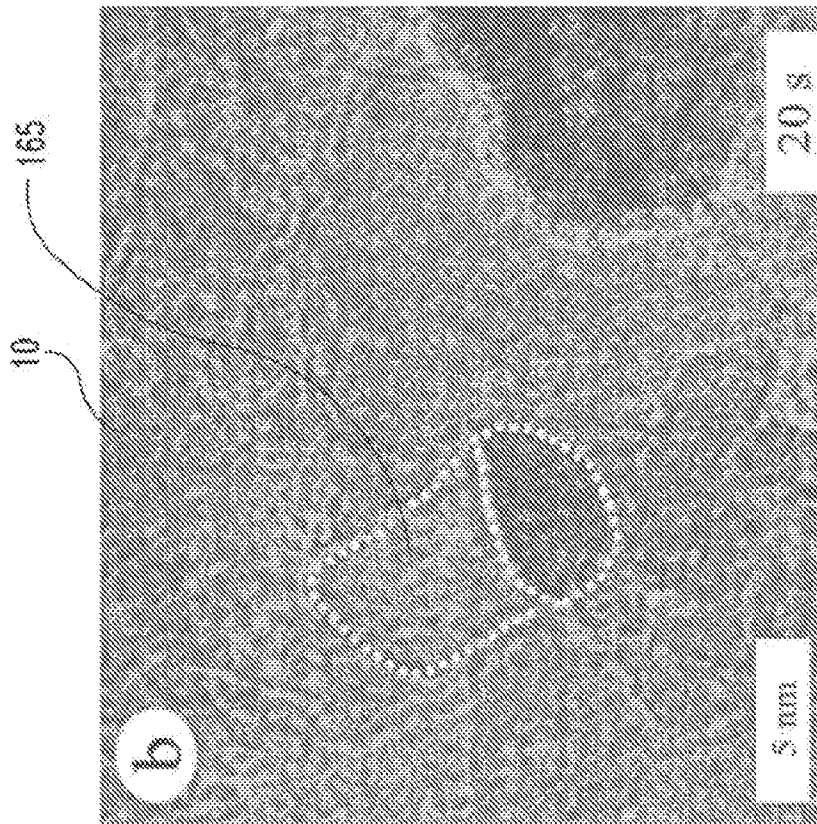


Fig. 7B

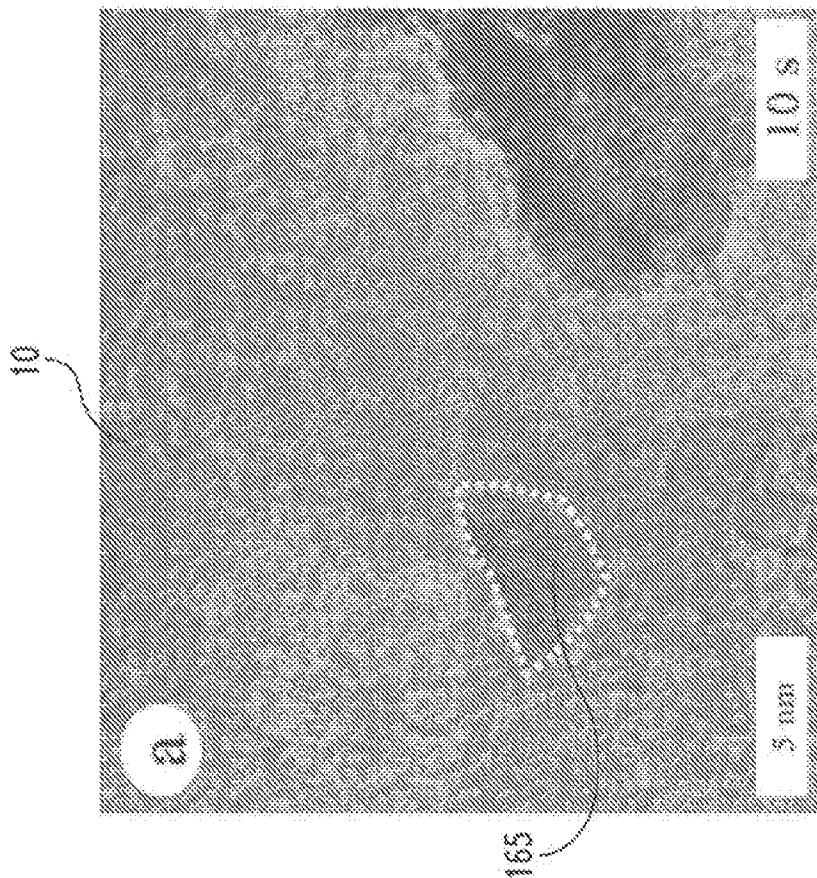


Fig. 7A

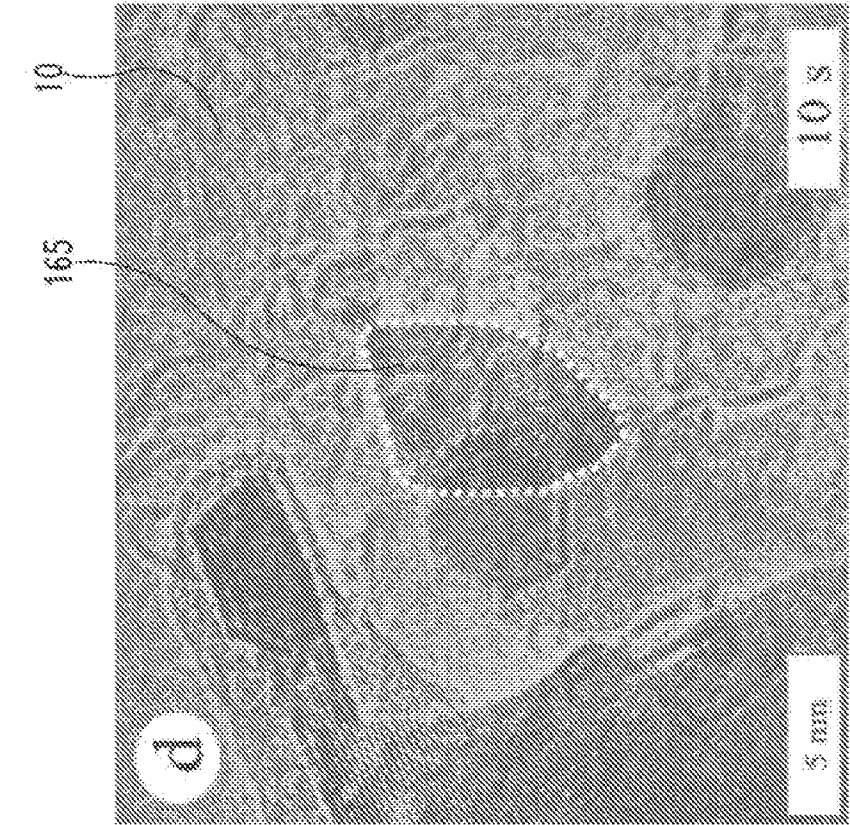


Fig. 7D

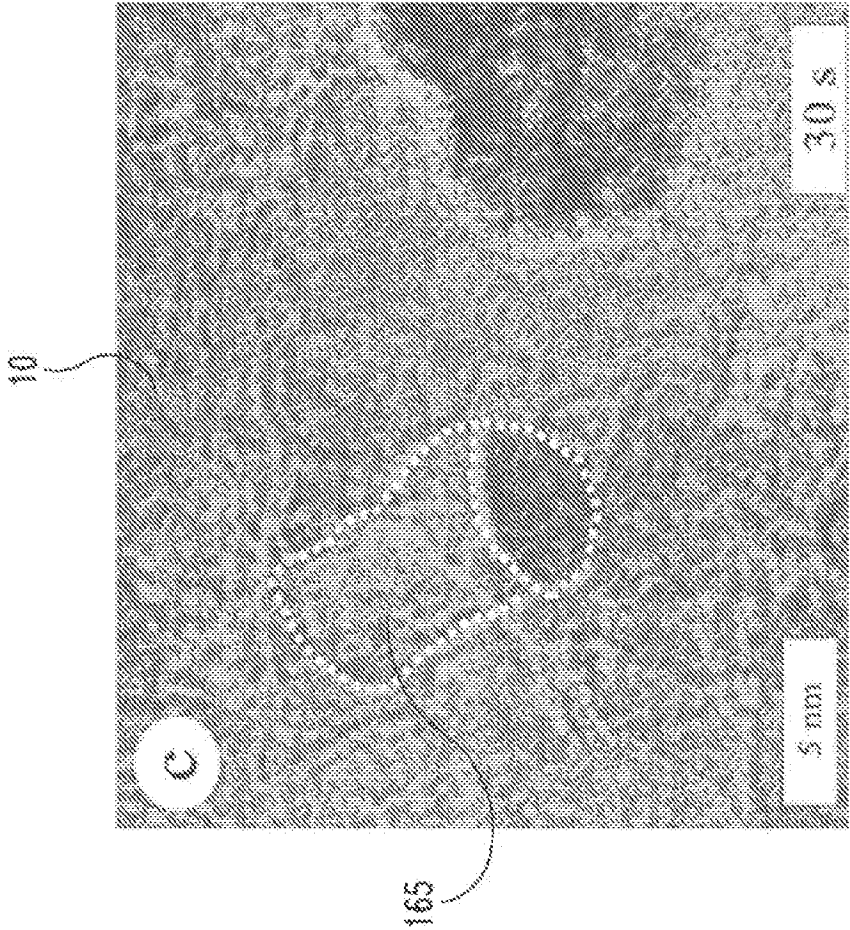


Fig. 7C

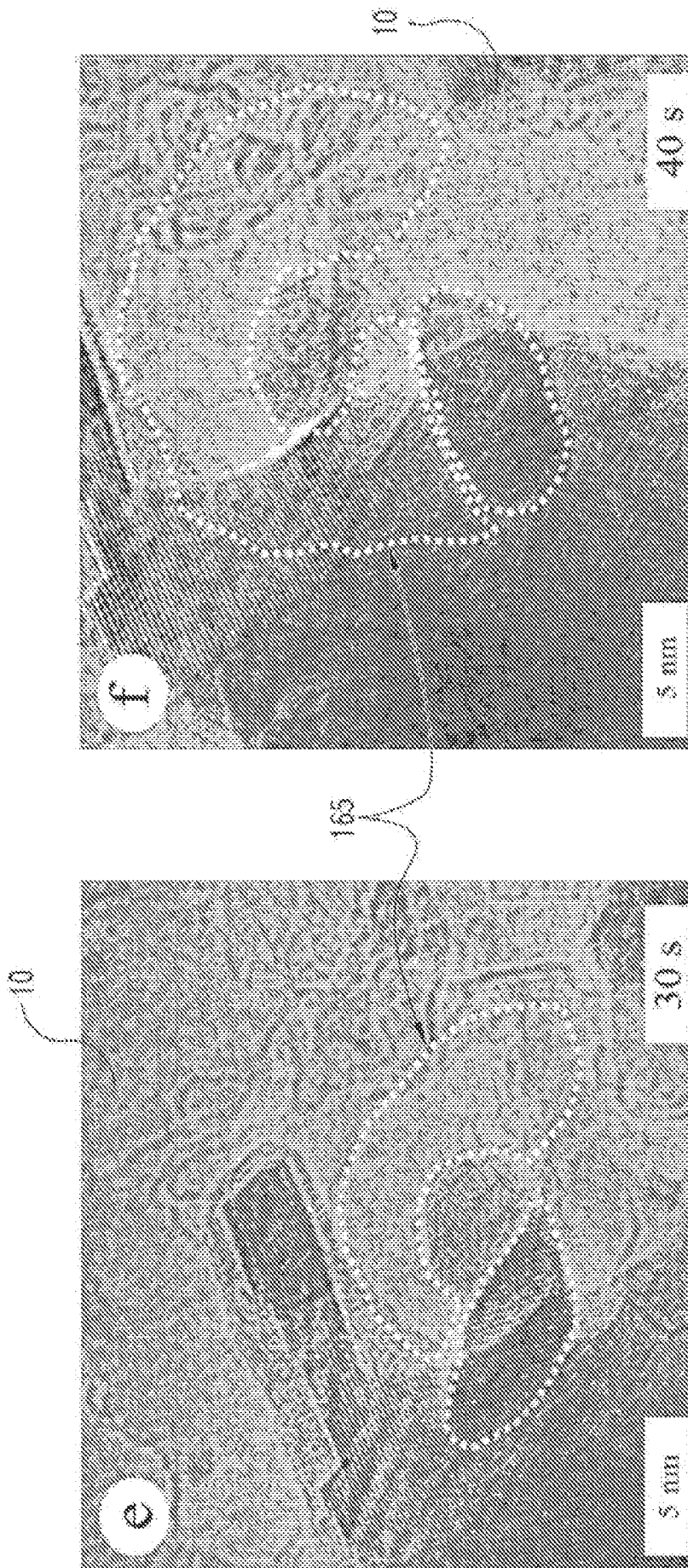


Fig. 7F

Fig. 7E

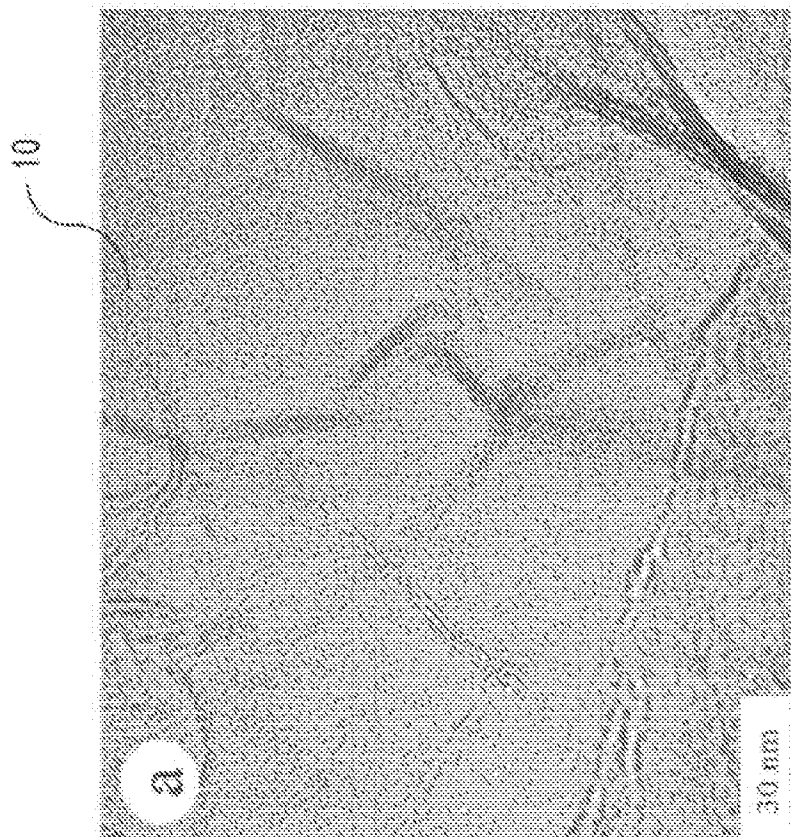


Fig. 8A

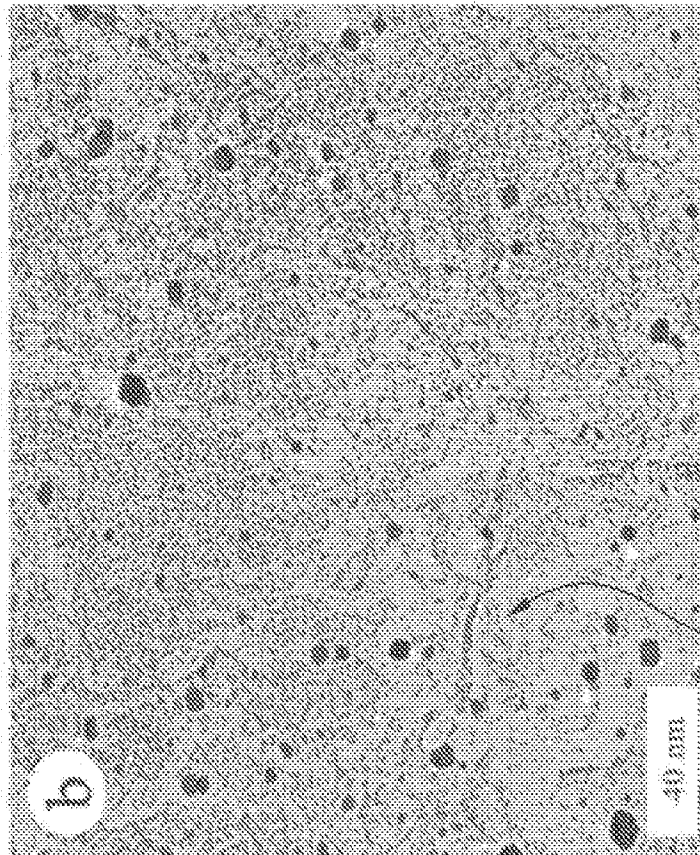
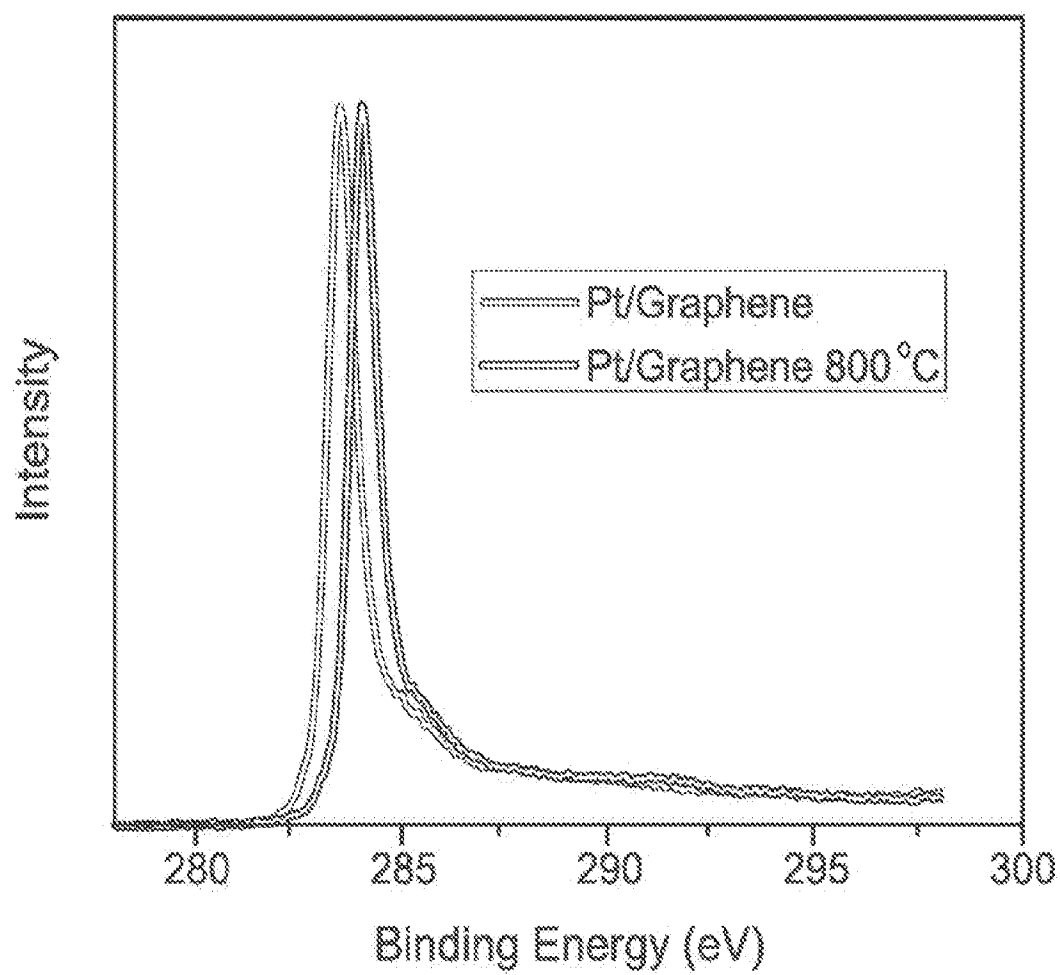
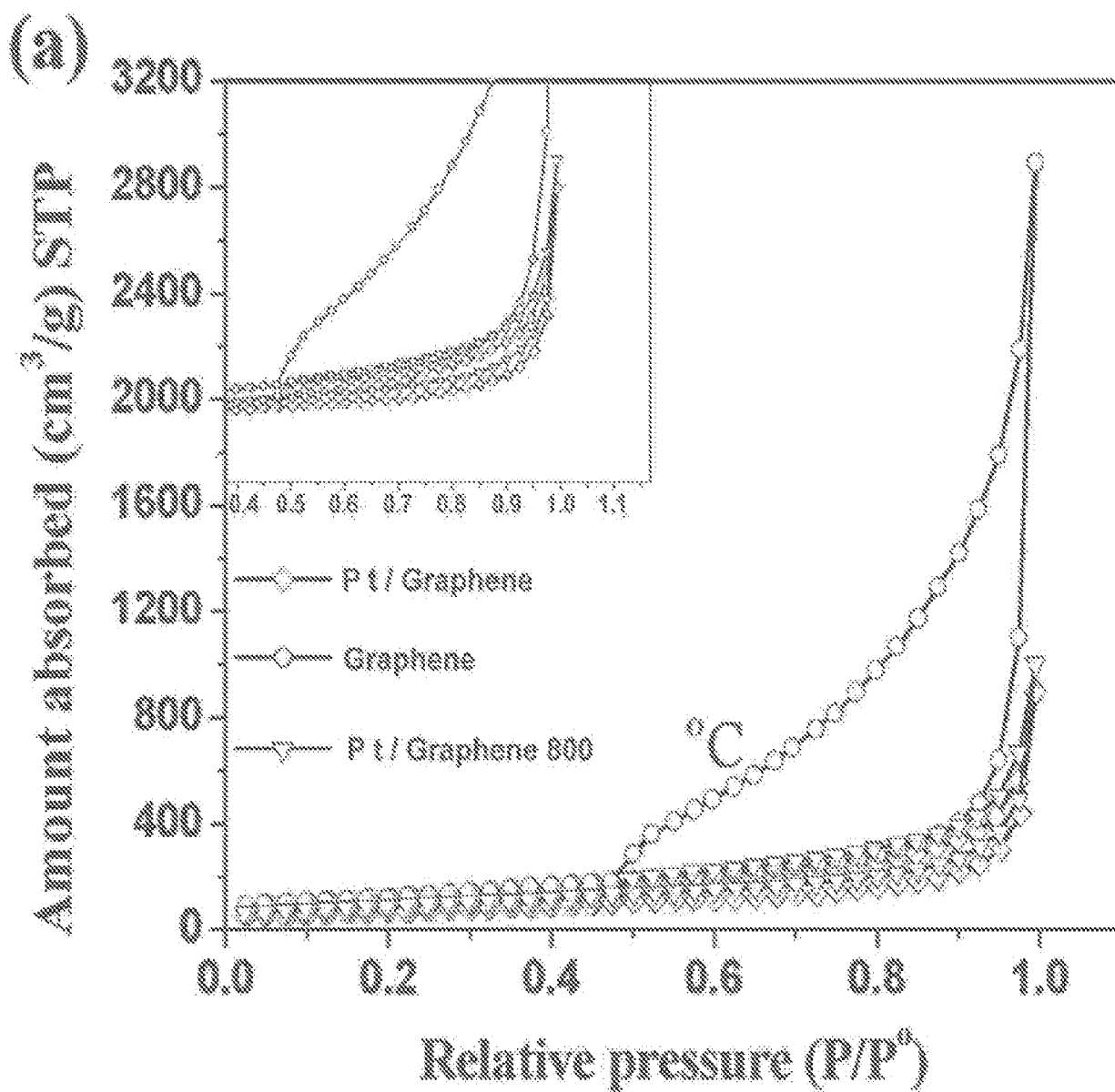
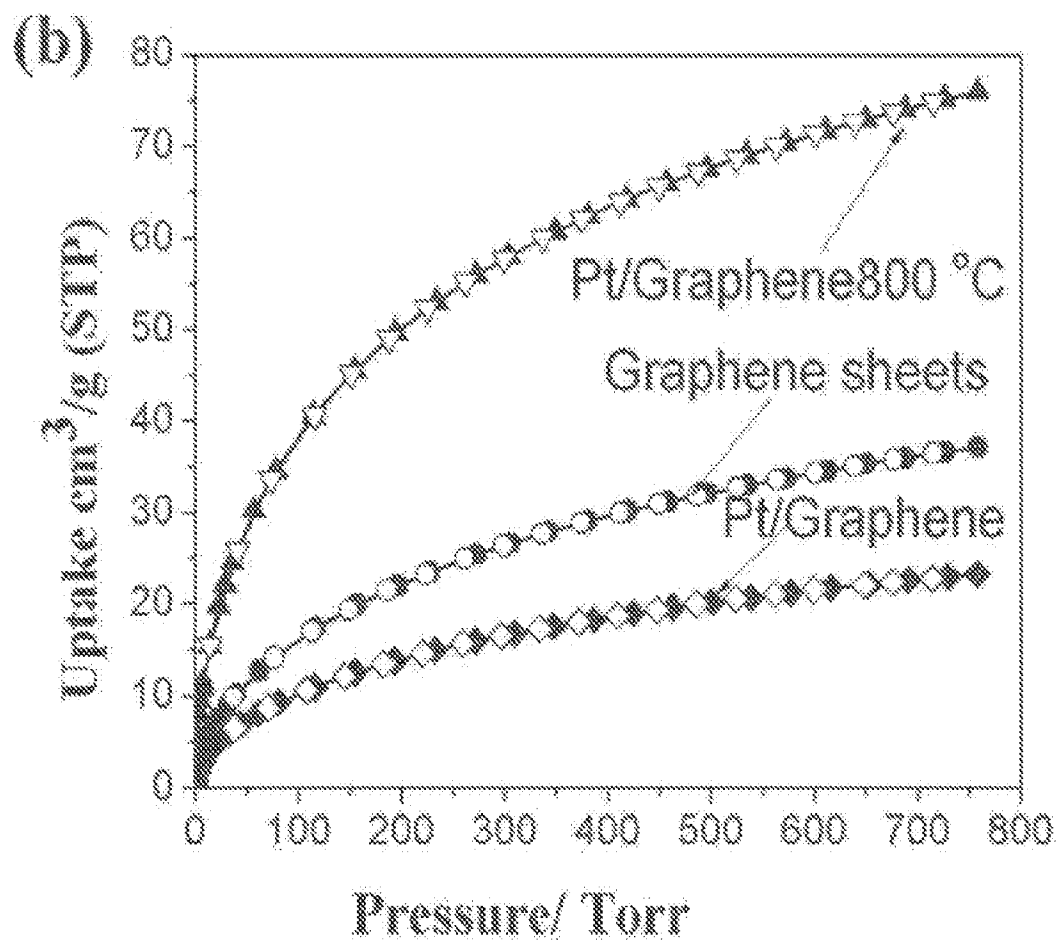
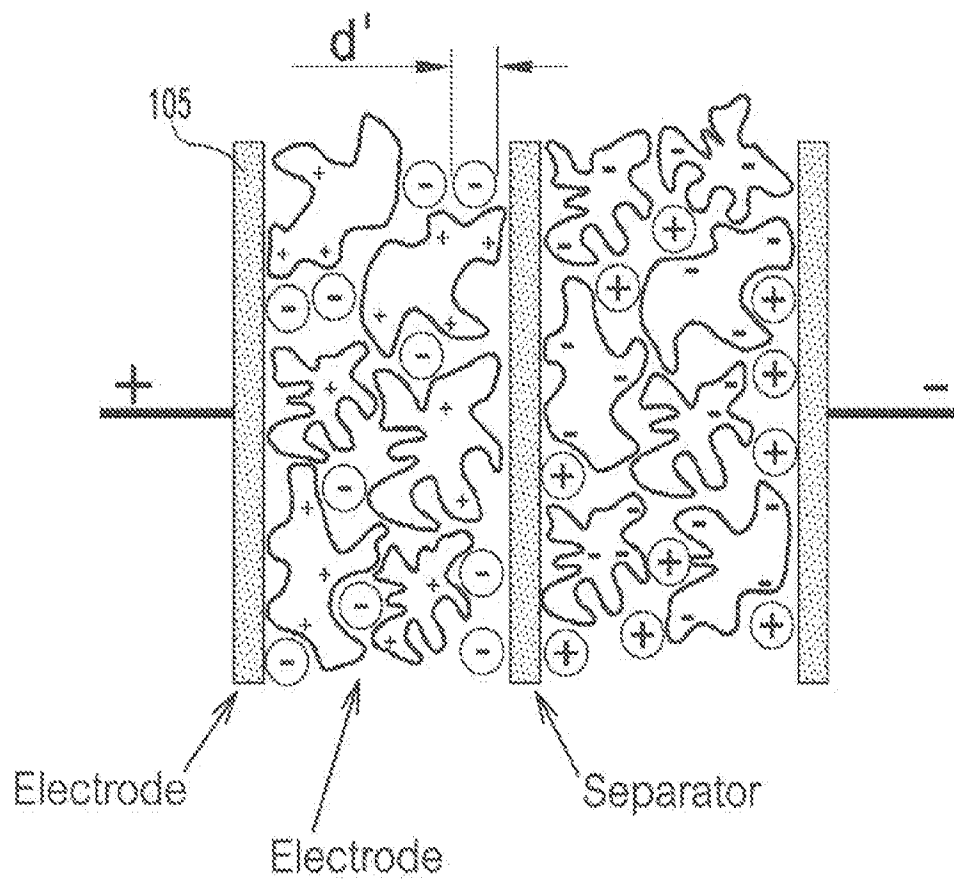


Fig. 8B

**Fig. 9**

**Fig. 10A**

**Fig. 10B**

**Fig. 11**

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 12/24894

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - H01M 10/00, 10/02 (2012.01)

USPC - 429/48; 252/506

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)

IPC(8)- H01M 10/00, 10/02 (2012.01);

USPC- 429/48; 252/506

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

USPC- 29/623.1, 320/162, 429/231.2, 429/332, 977/734, 977/773, 977/842;

Patents and NPL (classification, keyword; search terms below)

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

PubWest (US Pat, PgPub, EPO, JPO), GoogleScholar (PL, NPL), FreePatentsOnline (US Pat, PgPub, EPO, JPO, WIPO, NPL);
search terms: graphene, graphite, carbon, carbonaceous, particle, nanoparticle, energy, gas, storage, amorphous, etch, embed,
nanostructure, structure, Pt, platinum

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 2009/143405 A2 (SAMULSKI et al.) 26 November 2009 (26.11.2009), Fig. 4; para [0007], [0015], [0032], [0045], [0047], [0057]-[0060], [0068], [0069], [0088]-[0090]	1-21, 23-26
Y	US 2006/0165988 A1 (CHIANG et al.) 27 June 2006 (27.06.2006), para [0005], [0008], [0013], [0024], [0025], [0035], [0038], [0039]-[0041]	1-21, 23-26
Y	US 2010/0327847 A1 (LEIBER et al.) 30 December 2010 (30.12.2010); para [0047]-[0051]	22, 23
Y	US 2003/0098640 A1 (KISHI et al.) 29 May 2003 (29.05.2003), Fig. 14; para [0021], [0072], [0083], [0087]-[0090], [0100], [0144], [0146], [0149], [0167], [0175]	22, 23
Y	US 2009/0291270 A1 (ZETTL et al.) 26 November 2009 (26.11.2009), para [0009]-[0055]	1-26
Y	MCALLISTER et al. "Single Sheet Functionalized Graphene by Oxidation and Thermal Expansion of Graphite." Chemistry of Materials [online], Web Publication 25 May 2007 (25.05.2007) [Retrieved on 2012-05-15], Vol. 19, No. 18, pp. 4396-4404, Retrieved from the Internet: <URL: http://pubs.acs.org/doi/abs/10.1021/cm0630800 >, see entire document, especially Figs. 1-9	1-26

☐ Further documents are listed in the continuation of Box C.

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"P" document published prior to the international filing date but later than the priority date claimed

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

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"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

15 May 2012 (15.05.2012)

Date of mailing of the international search report

31 MAY 2012

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