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تحضيرٌ مبتكرٌ لتركيبة فلمٍ ثلاثي من: أكسيد الغرافين المُرجع/بولي أنيلين/أزرق بروسيا بطريقة طبقة فطبقة كالكترود مكثف فائق

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الملخص:

حضّر فيلم ثلاثي من الغرافين والبولي أنيلين وأزرق بروسيا.بطريقة مبتكرة بتقنية طبقة فطبقة على الكترود الغرافيت. بأربع خطوات: تقشير الكترود الغرافيت ثم ارجاعه كهربائياً ثم بلمرة الأنيلين كهربائياً كطبقة ثانية ثم ترسيب الطبقة الأخيرة من أزرق بروسيا كيميائيًا فوق الطبقات, للحصول على الفيلم الثلاثي المركب المسمى(LRGO/Pani/PB) .

اختبر الفيلم المركب الذي تم الحصول عليه بالقياس الطيفي (Uv-Vis, FTIR) كما أُخبرت خواصه الكهركيميائية بالقياس الفولطا أمبيرومتري الحلقي (CV) والشحن/التفريغ الغلفاني (GCD) وطيف المعاوقة الكهركيميائية (EIS). بلغت السعة الكهربائية النوعية للفيلم الثلاثي (718.9 F/g) عند كثافة تيار (0.1 A/g) و(401.8F/g) عند سرعة المسح (50 mV/s) وصل ثبات الفلم المركب حتى (97.1٪) بعد اخضاعه لـ (1000) دورة. تم إنشاء نموذج أولي للمكثف الفائق باستخدام كهرليت هلام الحالة الصلبة واختباره لإضاءة مصابيح LED أحمر وأبيض.

الكلمات المفتاحية: تقشير، ارجاع كهربائي، البوليمرات الناقلة، البولي أنيلين، أصفر بروسيا، أزرق بروسيا، مكثف فائق، طبقة فطبقة

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A novel synthesis of ternary composite film of: Reduced Graphene oxide /Polyaniline/Prussian Blue via layer-by-layer assembly for supercapacitor electrode

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Abstract:

An innovative method of preparing a ternary film of composite of Graphene, Polyaniline and Prussian blue on graphite electrode. The film has been manufactured by layer-by-layer technique.

The procedure has four steps: exfoliation then electroreduction of the graphite electrode, electro polymerization of aniline as second layer and finally deposition of Prussian blue layer chemically on top to obtain the ternary composite film (LRGO/Pani/PB).

The composite film obtained on graphite electrode was investigated by (Uv-Vis and FTIR) spectroscopy. Electrochemical properties of the electrode were investigated by cyclic voltammetry (CV), Galvanic Charge/Discharge (GCD) and Electrochemical impedance spectroscopy (EIS) techniques. The specific capacity of the ternary film reached up to (718.9 F/g at a current density of 0.1 A/g) and (401.8 F/g at 50 mV/s scan rate) with extended cycling stability up to (97.1%) after (1000) cycles. A prototype of supercapacitor was constructed with solid state gel electrolyte and tested for lighting both red and white LED.

Keywords: Exfoliation, Electroreduction, Electropolymerizing, Polyaniline, Prussian Yellow, Prussian Blue, Supercapacitor, Layer-by-Layer

1-INTRODUCTION:

Supercapacitors, which possess high storage capacity and prolonged cycle life compared to commercial batteries, play an important role as a promising energy storage system solving the challenging issues of fossil fuel exhaustions and climate changes [1]. Supercapacitors received considerable attention from both academic and industrial fields because they meet the need of a wide range of energy storage applications requiring short loading cycles with safety and stability such as power backup systems, portable electric devices, and electric vehicles [2–3]. To overcome the drawbacks of the low energy density of supercapacitors in practical applications, the pursue of electrode materials simultaneously with high energy density and prolonged cycle life are required for boosting energy storage performances [4,5]. Supercapacitors can be divided into two types depending on energy storage mechanisms. One is the electrochemical double layer capacitors (EDLCs), which store energy by physical adsorption/ desorption of ions at interfaces. Conductive and high-surface-area porous carbons are generally ideal electrode materials for EDLCs. The other is the Pseudocapacitors that store energy through reversible redox reactions of active materials. The Pseudocapacitors can deliver much higher capacitances than that of EDLCs but are greatly limited by poor electrical conductivity and easily damaged structures of the electrodes during cycles.

Most of the used common materials were Graphene which called 'super carbon' [6], defined as one-atom thick and two-dimensional sheet of carbon atoms fashioned in a hexagonal honeycomb lattice with a SP^2 hybridization [7] [8]. Graphene has been synthesized by two methods in general, Bottom-up method that graphene could be built from molecules example, chemical vapor deposition, epitaxial growth, and organic synthesis. with drawbacks include higher cost, Low yield and the difficulty to scale up compared with the second type that called top-down methods [9], Electrical exfoliation is one of last type of graphene preparation method. Electrical current causes the expansion of the graphite due to the intercalation of ions into graphite layers and the generation of tiny gas bubbles resulting from water splitting [10]. Electrical exfoliation is industrially attractive because it is an environmentally friendly (fewer organic solvents used) and versatile system, which enables the recycling of the unreacted materials. Additionally, it offers rapid graphene production and scalable number of products using variety of carbon as working electrodes such as graphite flakes and rods [11]. Many acids including HCl [12], H_2SO_4 [13], 14-and HNO_3 [15] have been tested as electrolytes. and found that H_2SO_4 is more effective in exfoliate graphene [16]. Moreover, sulphate salt-based electrolytes ($(NH_4)_2SO_4$, Na_2SO_4, K_2SO_4, etc.) were also tested [8][10]

Polyaniline is common material in this field as the oldest known electro conducting polymer [17]. The increased interest in polyaniline dates back to the discovery of its conductivity in the form of emeraldine salt and also its existence at different oxidation states. The fully reduced form refers to Leucoemeraldine base, half-oxidized form refers to emeraldine base, and fully oxidized form is Pernigraniline base [18]. Polyaniline can be obtained by Electrochemical polymerization of aniline monomer in acidic solution to form of green conductive emeraldine salt. Emeraldine salt can be easily oxidized to dark blue Pernigraniline salt or be transformed in reaction with alkali to violet Pernigraniline base. [19]

The last component in the composite was Prussian Blue, the pilot compound of diverse family of microporous inorganic solids which are called Prussian blue analogue. It has the general formula ($A_xP[R(CN)_6]_{1-y}.\ wH_2O$) where A represents a singly charged cation, often K^+ or Na^+, P and R are transition metals and y is the number of $[R(CN)_6]$ vacancies. Cyanide groups connect with P and R. The P atoms are coordinated to six nitrogen atoms, and the R atoms are coordinated to six carbon atoms, thus forming a framework with large voids. The cage-like structure exhibits wide channels, allowing for insertion of a wide range of intercalated ions. Prussian Blue Analogs (PBA) can be prepared from abundant non-toxic elements by simple and low-cost co-precipitation that is easily scalable. In addition to battery materials, PBA are promising electrocatalysts for water splitting [20-21]. The iron atoms are arranged alternately ferrous and ferric atoms, at the corners of a cubic lattice of 5.1 Å edge length, The CN groups lie at the edges of these small cubes. The alkali atoms occur at the centers of alternate small cubes [22].

In this work, we fabricated an integrated supercapacitor electrodes from ternary Layer-by-Layer composite materials on a graphite substrate. The method was exfoliation of graphite electrode using a fixed potential in two electrode-cell in 1M H_2SO_4 electrolyte to obtain local (in Sito) graphene oxide (LGO) layer, then electroreduction of mentioned electrode in three electrode-cell in same acidic electrolyte to produce local layer in sit of reduced graphene oxide (LRGO). (The resulting layer – graphene builds in substrate- has been studied via spectroscopy (UV-Vis and FT-IR)). Subsequently, polyaniline layer was electrodeposited by cyclic voltammetry technique in the potential range between (-0.2 to 1.2 V). The last layer of Prussian Blue was chemically deposited film via Prussian yellow by immersing the electrode in the Prussian yellow solution (mixture of ferric nitrate and potassium hexacyanoferrate) for few seconds to obtain Prussian Blue layer on top as explained in schematical diagram in Fig (1).

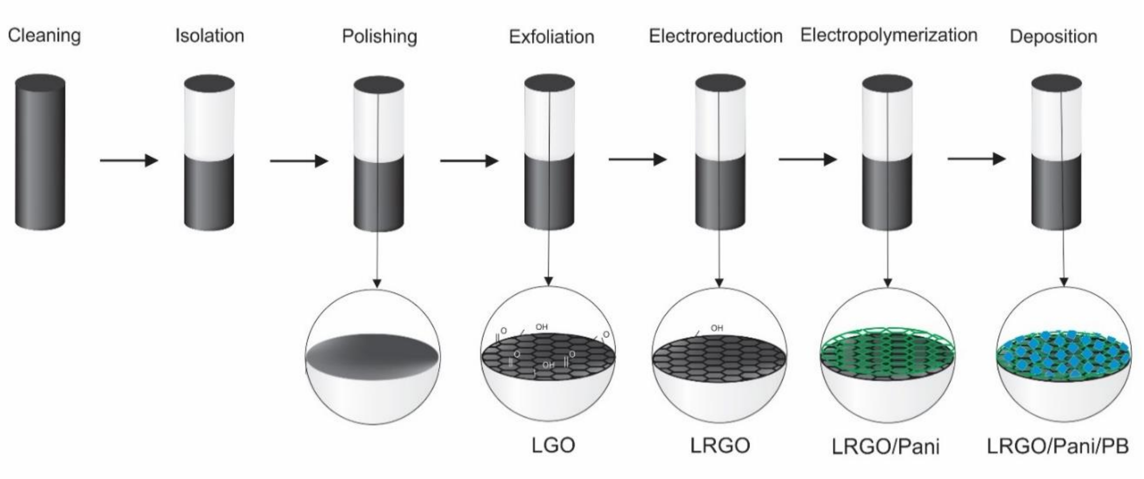

Fig (1): Schematic diagram of the main steps for supercapacitor electrode preparation

The electrochemical properties of ternary composite film LRGO/Pani/PB were compared to its components, using CV and GCD techniques. Which reached to compute the specific capacity. It also studied the impedance of charge transport across the electrolyte interface by EIS technique.

2.Experimental:

graphite electrode rod of 0.5cm diameter was cylindrical surface isolated. The circular surface was polished mechanically. Sulfuric acid, potassium chloride, Iron (III) nitrate and Potassium hexacyanoferrate (III) were lab grade and from Panreac, BHD, Merck, Reidel respectively. Aniline from Sigma distilled twice before use. The exfoliation of graphite electrode using (Sinometer HY5003) power source. UV-Vis and FTIR spectrums were recorded using spectrophotometers (SINCO-S3100) and (Shimadzu - IRSpirit) respectively. Electrochemical measures (CV, GDC and EIS) were carried out using IVIUMSTAT. XR station. All applied potential were taken against the Ag/AgCl reference electrode.

3-RESULTS AND DISCUSSION:

3-1 preparation of ternary LRGO/Pani/PB film:

The substrate made of graphite electrode was exfoliated in two electrodes cell (the anode was graphite electrode and Pt wire was the cathode electrode), by applying a constant potential of 6 V in 1 M H_2SO_4 electrolyte up to 60 seconds. Sonication of the electrode was carried out for 5 min in 10 ml of distilled water to remove crusts (this solution was collected for spectrophotometry measurements). We assumed that little amount of LGO resulted in exfoliation processes. It has to be reduced to a LRGO by cyclic voltammetry, in three electrode cell: Pt wire was the counter-electrode, LGO was working electrode, Ag/AgCl was reference electrode. The potential range was between (0, -1.5 V) in 1M H_2SO_4 electrolyte, at 50 mV/s scan rate, three cycles.

The Fig (2-A) was explained the voltammograms response of electroreduction of LGO traces to LRGO layer. The adsorbed oxygenate groups into electrode surface, begin to reduce after potential value -0.7 V (in the negative direction) up to -1.5 V. That clear in the first cycle. Leading to an active reduction of the LGO to obtain LRGO layer.

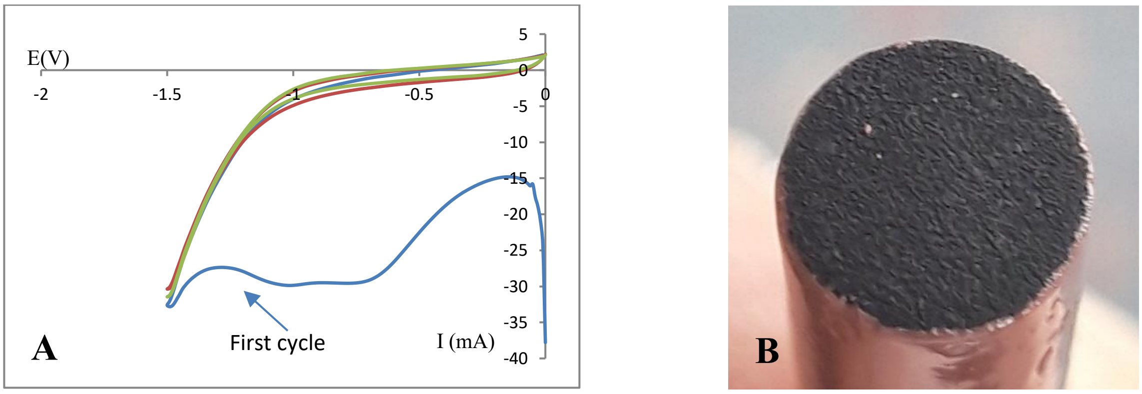

Fig (2): (A)- voltammogram response of electroreduction of LGO in 1M H_2SO_4 electrolyte, in three electrodes cell. (B)- real picture of LRGO.

Next, a second layer of polyaniline (Pani) was deposited on LRGO electrode, by electropolymerization of 0.1 M of aniline in 0.5 M of H_2SO_4 as electrolyte in three electrode cells: Pt wire was the counter-electrode, Ag/AgCl was the reference electrode and LRGO was the working electrode, in potaintial range (-0.2 , 1.2V). With of 50 mV/s scan rate, eight cycles. Figure (3-A) and Figure (3-B) represented the voltammograms response of aniline electropolymerization on graphite electrode and the LRGO electrode respectively in the same conditions.

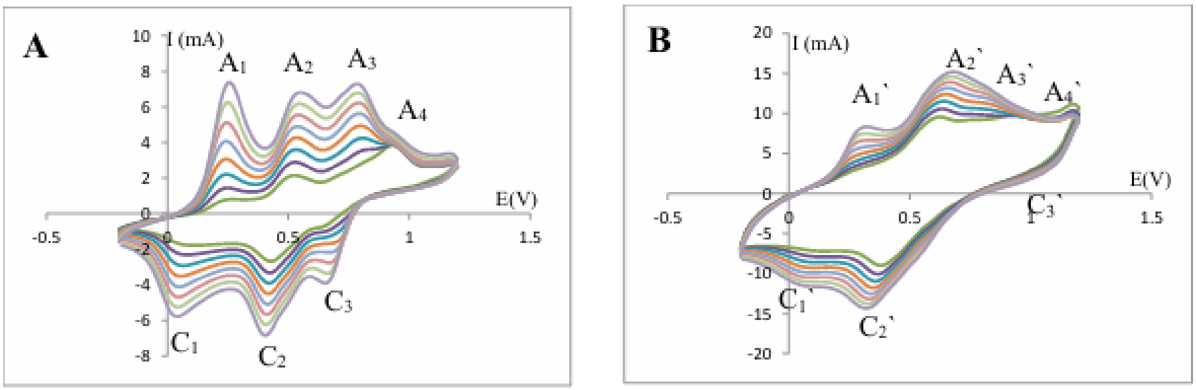

Fig (3): voltammogram response of electropolymerizing Pani on (A)- graphite electrode. (B)- LRGO electrode in three electrodes cell.

Fig(3-A) illustrated CVs curves of graphite electrode. It seemed as a typical Pani electropolymerizing curve, with three sharp pairs of conspicuous peaks (pseudocapacitive behavior). The first A_1/C_1 pair at approximately 0.2 V corresponds to a reversible redox reaction from Leucoemeraldine (insulating form) to Emeraldine (conducting form) [23]. The next pair of A_2/C_2 peaks occurring at about 0.5 V corresponds to a redox reaction of Pani degradation (transition from benzoquinone to hydroquinone) [24]. The other set of peaks A_3/C_3 at 0.8 V corresponds to the oxidation of Emeraldine in the fully oxidized Pernigraniline state (non-conductive) [22]. The last irreversible peak at 0.9 V (A_4) is the oxidation of aniline monomers which initiates the polymerization reaction [22]. The CV curves of the LRGO electrode in Fig (3-B) seemed as a semi rectangular shape distinguished with broad peaks (super capacitive behavior). These remarkable peaks pairs at around 0.2, 0.5 and 0.8V (A_1\`/$C_1$\`, A_2\`/$C_2$\` and A_3\`/$C_3$\`) corresponds to Pani transformations and irreversible peak at 0.9 V (A_4\`) corresponds to the oxidation of aniline. And the resultant current from the LRGO electrode was about 15 mA whereas it was about 8 mA in the graphite electrode.

Last layer on top of LRGO/Pani electrode was deposited by immersion into a fresh solution of 0.1 M Prussian yellow for 30 s which combined two equal volumes of 0.2 M $Fe(NO_3)_3$ and 0.2 M $K_3Fe(CN)_6$. The blue coat could immediately naked eye observed due to formulation Prussian Blue layer. Polyaniline's presence accelerates Prussian blue deposition. A 10 s of repeatedly washing with distilled water followed each step and dried in 50 ºC and store in desiccator.

It is difficult to get a multilayered film with these three materials (LRGO, Pani and PB) in other arrangement, because the local graphene layer should be the first layer, and the PB layer must be next to Pani layer depending on redox reactions between Pani/Ani with PY/PB.

3-2 Structural study of ternary LRGO/Pani/PB film:

To improve presence of LGO and its conversion to LRGO by electroreduction, a spectrophotometric study was achieved on three solutions: a- eliminated solution of LGO electrode by 15 min ultrasonication. b- LGO carried out by surgeon's blade and ultrasonication. c- eliminated solution of LRGO electrode by 15 min ultrasonication. the three spectra were indicated in Fig (4-A).

the absorbance of a and c solution in Fig (4-A) shows absorbent peak at 238 nm meet to $\pi - \pi^*$ transition and wide shoulder at 305 nm meet to $n - \pi^*$ transition related to graphene oxide [25]. This absorbance peak will shift to longer wavelength after electroreduction to absorbance at 270 nm corresponding to the $\pi - \pi^*$ transition (RGO on electrode named in figure(4-A)) [27].

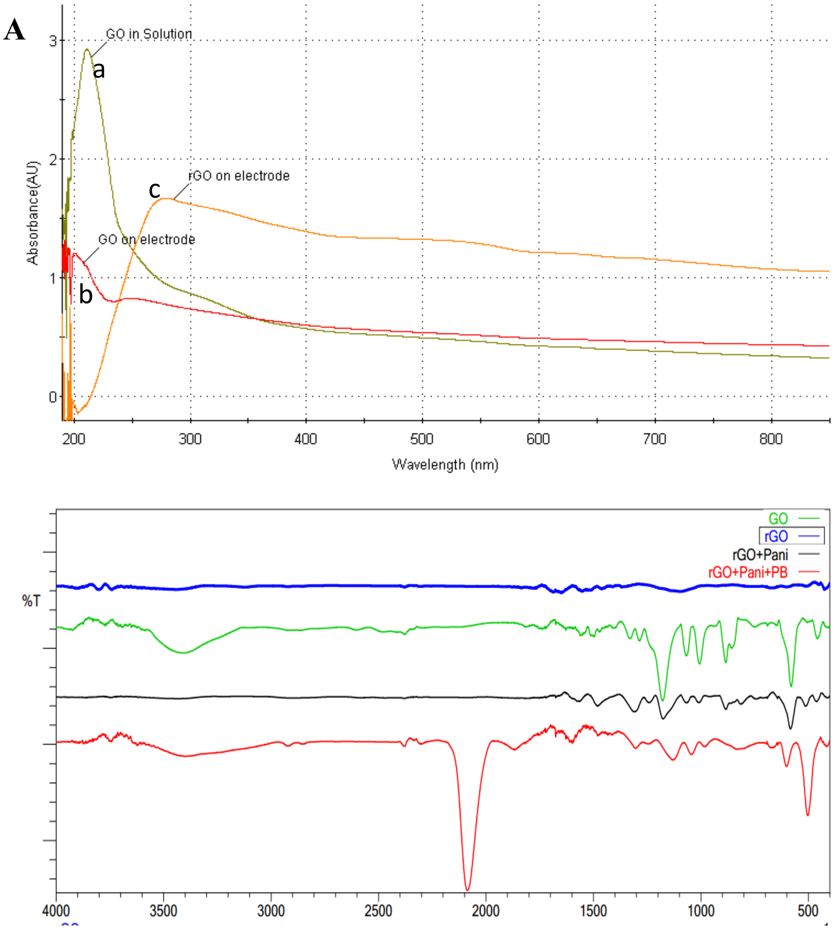

Fig (4) :(A)- -UV-Vis absorbance spectra of (GO in solution) removed by sonication and (GO in electrode) removed by surgeon blade, and (RGO on electrode) removed by sonication. (B)- FT-IR spectra of GO, RGO, LRGO/Pani and LRGO/Pani/PB electrodes.

For more details a chemical composition of the ternary LRGO/Pani/PB film was recorded by FT-IR spectroscopy between (400 – 4000 cm^{-1}). Fig (4-B) shows the FTIR spectra of LGO, LRGO, LRGO/Pani and LRGO/Pani/PB films after film removal and drying it at 70ºC in vacuum oven over night.

As can be seen in Figure (4-B), the FT-IR spectrum of GO (green line) shows absorption band at 1725 cm^{-1} due to the C=O stretching in the -COOH groups. Vibrational bands due to carboxy (C-O; 1406 cm^{-1}), epoxy

(C-O; 1220 cm^{-1}), and alkoxy (C-O; 1058 cm^{-1}) groups situated at the edges of the GO nanosheets were also found, as reported elsewhere [26].

Almost all these bands were weakened even disappear after electroreduction (blue line) in LRGO layer evidence to the efficiency of electroreduction. In another spectrum LRGO/Pani film (black line) Compared with LGO spectrum, a several new bands attributed to Pani polymer appeared in the spectrum of LRGO/Pani Notably, two new bands around 1600 and 1461 cm^{-1} are attributed to the vibrations of C=N and C=C, respectively. Additionally, a stretch band assigned to C-N also appears at 1300cm^{-1}. A band at about 800 cm^{-1} could be attributed to the C-H out-of-plane bending vibrations, while the many bands ranging from (800 - 580 cm^{-1})can be assigned to the vibrations of the C-H bonds in the benzene rings. The appearance of the quinonoid and benzenoid ring vibrations (C=C stretching deformations) at about 1564 and 1461 cm^{-1} respectively. clearly indicates the presence and formation of Pani on the graphene surfaces. The characteristic band attributable to the N-Q-N-Q stretch of the quinonoid ring was also found at around 1144 cm^{-1}, which clearly supports our hypothesis that the Pani has been covalently grafted onto the surface of the LRGO sheets [28].

Additional strong intensity band was observed in last spectrum LRGO/Pani/PB (red line) at 2090 cm^{-1}, which is ascribed to the stretching transition band of the CN group in the Fe-CN.

3.3. Electrochemical performance study of ternary LRGO/Pani/PB film:

To investigate impact of LGO and LRGO in graphite electrods a cyclic voltammetry was performed in three electrode cell: pure graphite, LGO or LRGO electrodes as a working electrode. Pt wire was counter electrode. and Ag/AgCl was reference electrode. The electrolyet was 0.1 M KCl+1 M H_2SO_4 . At 50 mV/s scan rate. This considered as additional evidence of the efficiency of these two successive steps: exfoliation and reduction.

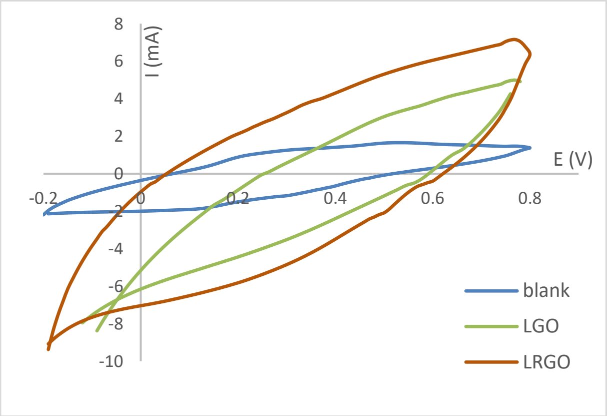

Fig (5): Voltammograms response of graphite electrode (blue line), exfoliated graphite LGO electrode (green line) and modified LRGO electrode (red line). in 0.1 M KCl+1 M H_2SO_4.

The CVs curves in Figure (5) had the same rectangular shape without remarkable peaks that serve ECDL type in the absence of faradic reactions. The enclosed area become larger with the arrangement: graphite<LGO<LRGO electrodes.

In order to follow the effect of each layer component, a comparative study was performed between the single layer component and the bilayers of two components and the ternary film of three components. Voltammogram responses were carried out in three electrode cell the Pt wire was the auxiliary electrode. The electrolyte was 0.1 M KCl+1 M H_2SO_4 between -0.2 and 0.8V against Ag/AgCl as reference electrode at 50 mV/s scan rate, as explained in Figure (6-A, B, C).

Figure (6-A) describes the CV curve of Individual component (LRGO, Pani and PB) films. The smallest closed area (blue line) has an $a_1 \approx 0.2$ V redox peak corresponding to the Prussian blue transformation from Prussian white (PW) to Prussian blue (PB) and vice versa at c_1. The pure Pani film (green line) has the highest area with three pairs of typical peaks in a_2/c_2, a_3/c_3 and a_4/c_4 corresponding to transformation of Leucoemeraldine to Emeraldine and Emeraldine to Pernigraniline. And at last, LRGO curve (black line) has no peak of note due to ECDL behavior.

The CV curves of the Bilayer films in Figure (6-B) have sum properties of two components which have made with additive properties in particular the specific capacities.

The changes in specific capacity and shape of CVs were clearly indicated in Figure (6-C) which illustrated the ternary film developing LRGO, LRGO/Pani and LRGO/Pani/PB films. Ternary films appeared the largest closed area and specific capability. from the integration of the confined area in CV plots will estimate charge value, then the specific capacity according to equation (3) [27]:

$$C_{sp} = \frac{1}{m\times S\times \Delta V}\int_{V1}^{V2} IdV = \frac{Q}{m.s.\Delta V}$$

Where: m is the mass (g) of (LRGO/Pani/PB). ΔV is the potential window (Volt). The s is the scan rate (V/s). and I is the instantaneous charge current (A) in a given potential. Q is the charge (AV). The integrated area value for ternary film was 0.0160 (AV) calculated by origin lab software. and the specific capacities calculated of LGGO, LRGO/Pani and LRGO/Pani/PB films were 183.6, 386.3 and 401.8 F/g respectively.

To check the stability of the LRGO/Pani/PB ternary film, a prolonged cycling was carried out in a potential window of -0.2 to +0.8 V at scan rate of 50 mV/s as Fig (6-D). Remarkable long-term cycling stability was appeared, retaining 97.1% of its original specific capacity after 1000 cycles. This excellent stability results from a high degree of redox reversibility. Which could be attributed to the electrostatic attraction between differently charged particles (BP and Pani). The Pani chains conductive polymer stabilizes PB nanoparticles as a framework, and maintain redox centers stable mechanically. The Pani also contribute in redox reaction that facilitate the charges and electron shuttle along its backbone [24].

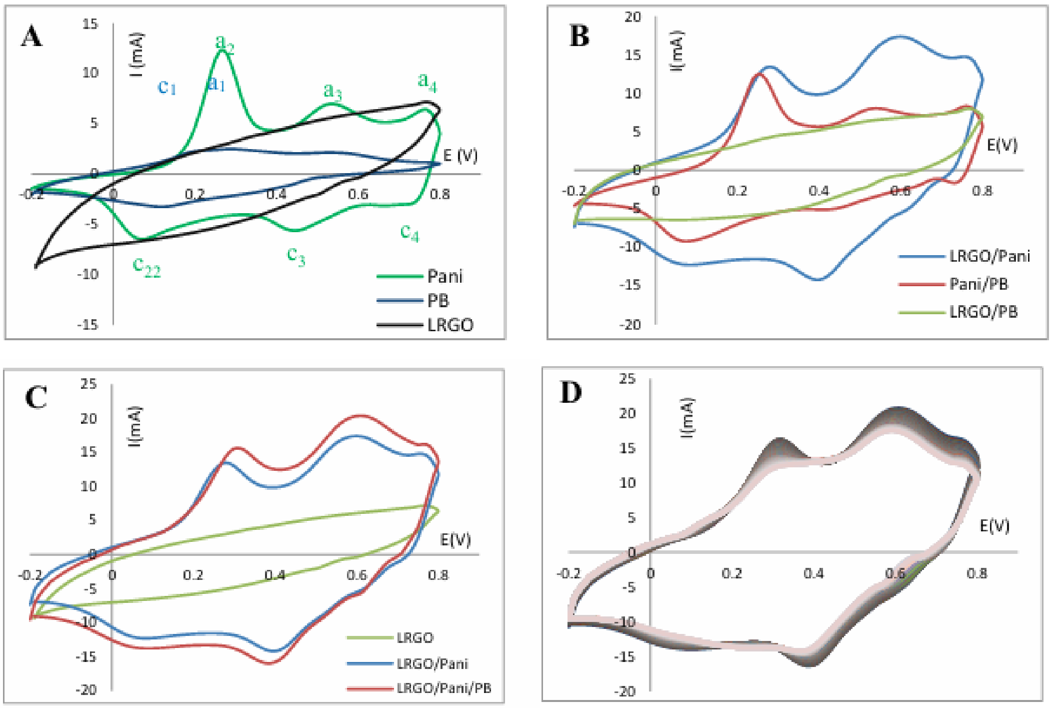

Fig (6): Voltammograms response of A- single layer of LRGO, Pani and PB. B- bilayers of two components of (LRGO/Pani, LRGO/PB and Pani/PB). C- ternary layer of (LRGO/Pani/PB overlaid. in 0.1 M KCl+1 M H_2SO_4. D- Voltammograms response of LRGO/Pani/PB film in 0.1 M KCl+1 M H_2SO_4 for a1000 cycles. were carried out mixture of 1M H_2SO_4 in 0.1 M KCl

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Fig (7-A) shows the CVs curves of ternary film LRGO/Pani/PB at various scan rates. The shape of these curves remained unchanged, indicating good capacitive behavior and high capability. The increased scan rates have a direct effect on the diffusion of H^+ and K^+ ions which do not penetrate the outer surface of the films. And the material interior in deep of pores will contribute in small amount in the capacity and decreasing it [28].

In order to study the electrochemical kinetics of charge/discharge process. The current values of anodic peaks current were plotted versus both the scan rates (mV/s) and the square root of scan rate $(mV/s)^{-1/2}$ as in Fig (7-B) and in Fig (7-C) respectively. Fig (7-C) was more linear, proving that the redox process is controlled by adsorption of ions to the surface material [29].

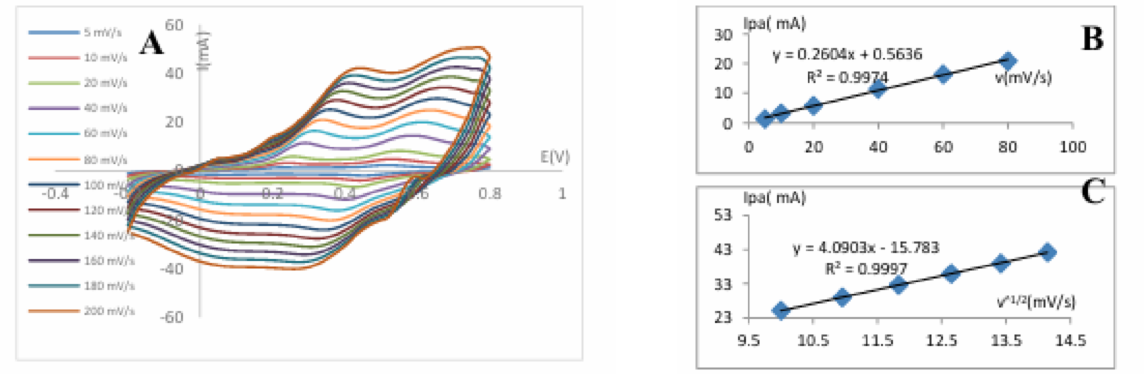

Fig (7): A- voltammetric responses of LRGO/Pani/PB at different scan rates 5mV/s to 200mV/s. B-The relationship between the anodic peaks current density (Ipa) and scan rate ν(mV/s). C- The relationship between the anodic peaks current density (Ipa) and square root of scan rate $\nu^{1/2}$ (mV/s). All voltammograms

To reveal the electrochemical performance of individual films (LRGO, Pani and PB). and Bilayer films (LRGO/Pani, LRGO/PB and Pani/PB). and Ternary film of LRGO/Pani/PB. Galvanostatic Charge-Discharge (GCD) curves have been reported at a fixed current density (1 A/g) and vary from (0.3 - 5 A/g) current density, in (1 M H_2SO_4 and 0.1M KCl) electrolyte. All GCD curves has symmetrical semi linear forms. with distinct thumps which indicate that the specific capacitance was yielded of both pseudo capacitance and electrical double layer behavior.

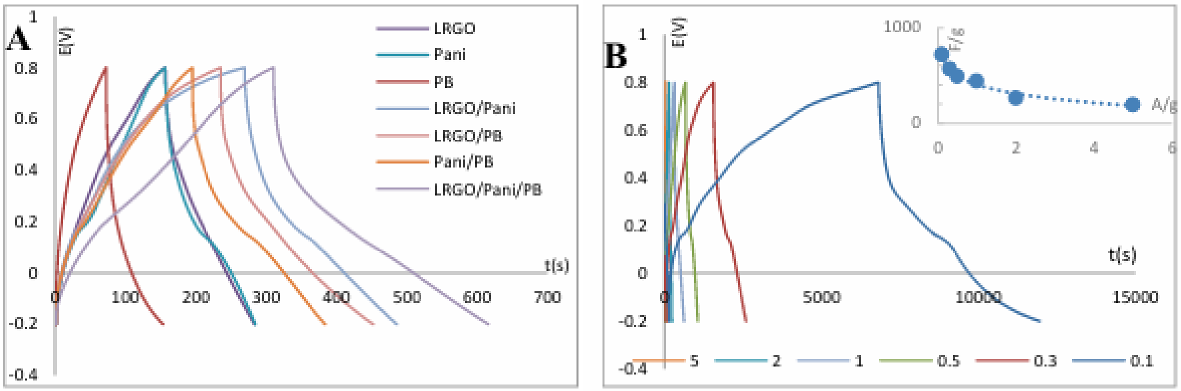

Fig (8): A-Galvanostatic Charge/Discharge curves of one layer of (LRGO, Pani and PB), bilayer of LRGO/Pani, LRGO/PB and Pani/PB **and ternary film of LRGO/Pani/PB @ 1 A/g current density. B- Galvanostatic Charge/Discharge curves of Ternary film of LRGO/Pani/PB at different current density 0.3 A/g to 5 A/g. The electrolyte was (1M H_2SO_4+0.1M KCl)**

The specific capacitance was calculated from discharge period in GCD curves depending on the equation: $C_{sp} = \frac{I.t}{m.\Delta E}$.[26] Where: I is the discharge current (A). t is the discharge time (s). ΔE is the potential window (V). m is the mass of the active material (g). The results were 195.7, 200.6, 137.1, 319.1, 277.1, 270.6 and 444.6 F/g for LRGO, Pani, PB, LRGO/Pani, LRGO/PB, Pani/PB and LRGP/Pani/PB films respectively, applying 1 A/g current density as Fig (8-A) explained which be considered as further evidence for success of multilayer preparation supercapacitor.

With respect to the (IR drop) of the LRGP/Pani/PB which has a minimum value reflecting the fact that the internal resistance between three layers was negligible. This is beneficial in energy storage because less energy is wasted as unwanted heat during the charge-discharge process.

Fig (8-B) shown GCD curves of ternary LRGO/Pani/PB film at different current densities from 0.1 to 5 A/g which has maintained the same shape. The minimum IR drop can also be seen in the current density of 5 A/g. demonstrate that the synergistic effect of the three layers has enhanced specific capacity and rate capability at high current density. It was revealed that the specific capacitance of film decreased with increasing applied current density, the values were 718.9, 569.1, 493.4, 444.6, 265.7 and 197.1 F/g for 0.1, 0.3, 0.5, 1, 2 and 5A/g applied current. it was clear that the highest value related with the lowest applied current as Fig (8-B inserted) explained.

Electrochemical impedance spectroscopy is a powerful informative technique to evaluate properties of the electrical conductivity and charge transport through the interfaces. EIS collected in frequency range 10 mHz – 100 kHz in electrolyte of 1 M H_2SO_4 + 0.1 M KCl. The data were analyzed using Nyquist plots as shown in Fig (9).

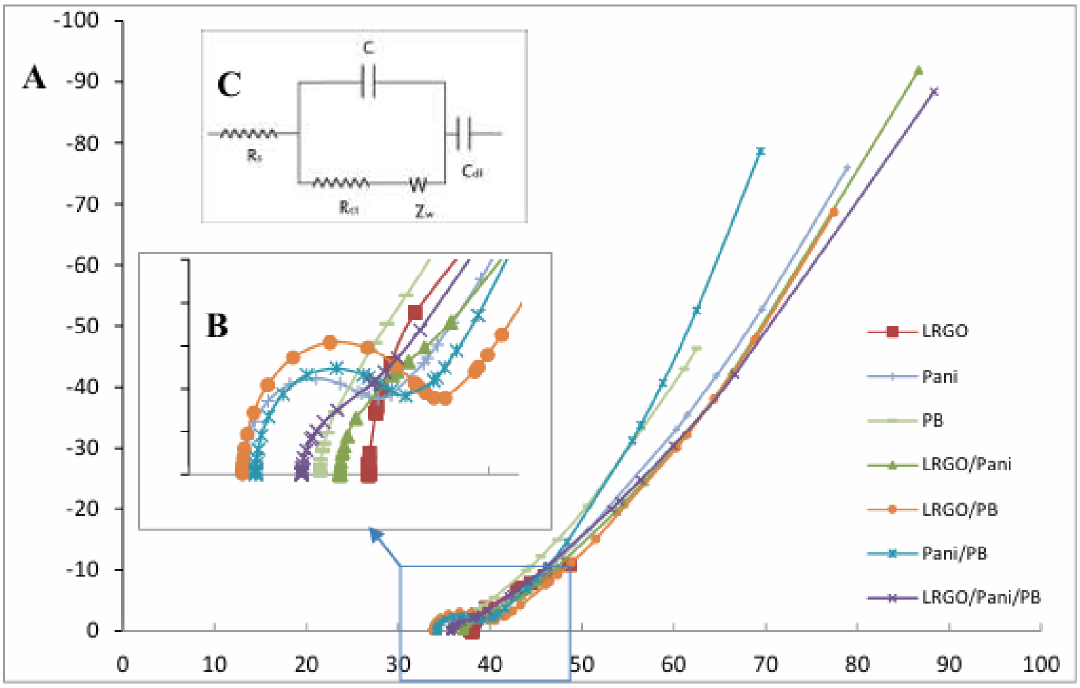

Fig (9): A- EIS curves of one layer, bilayer and ternary layer film in 1M H_2SO_4+0.1M KCl. B- zooming on high frequency region C- the equivalent circuit.

All films exhibited two distinct regions, a semicircular arc in the high frequency region and a nearly straight line in the low frequency region.

To further understand the behavior, the equivalent circuit modeling was established, as presented in (inside) Fig (9-C). The intercept at the real axis in the high frequency region, represents the equivalent series resistance (Rs), associated with the sum of the ionic resistance of the electrolyte, the intrinsic resistance of active material and the contact resistance.

Table (1): resistance values of different films.

	LRGO	Pani	PB	LRGO/Pani	LRGO/PB	Pani/PB	LRGO/Pani/PB
Rs (Ω)	38.0	33.8	36.4	37.0	33.8	34.2	35.8
Rct (Ω)	6.8	4.0	2.5	2.6	5.8	4.5	1.8

The values of the resistance Rs converged to each other for all films. But the least value was in the pure Pani and LRGO/PB film. The charge transfer resistance (Rct) related to internal resistance caused by the Faradaic reactions which can be obtained from the diameter of the semicircles in magnified curve in Fig (9-B). We found that (Rct) values -table (1)- were decreased with ternary film 1.8 Ω, evidence of the synergistic effect of fast charge transfer of ternary LRGO/Pani/PB film.

3.4. Application of ternary LRGO/Pani/PB film:

Three real supercapacitors of solid state devices were made by coupling six prepared LRGO/Pani/PB electrodes (5 mm×10 mm). The separator soaked with solid gel electrolyte consists of (10 % PVA + 0.1 M KCl in 1 M H_2SO_4).

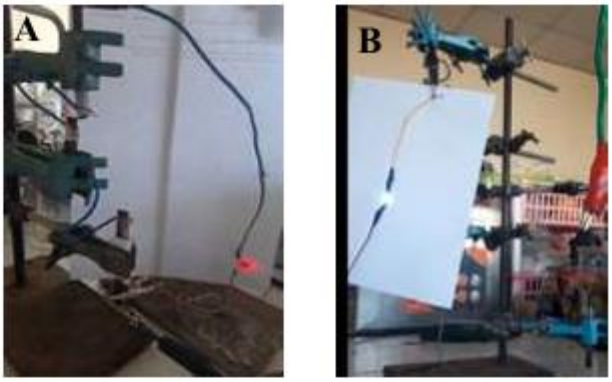

Fig (10): real photos of three devices connected in series lighting A- red LED. B- white LED.

These devices should be fully encapsulated and leak-free. these three devices were serial connected and charged about 5 V for 10 s. the connecter devices could light a red LED (2.4 V) to more than 120 s and a white LED (>3 V) to more than 90 s as the figure (10-A, B) appeared.

4. CONCLUSIONS

A ternary film of in Sito reduced graphene oxide, Polyaniline and Prussian Blue have been synthesized by modifying graphite substrate using electrochemical/chemical method:

1- Exfoliation and reduction of graphite electrode in acidic media and investigation whether a species of reduced graphene was presented. This is considered the first layer LRGO.
2- Electrodeposition of Pani eight cycles over LRGO by cyclic voltammetry.
3- Deposition of last layer by immersion LRGO/Pani electrode in solution of $Fe(NO_3)_3 + K_3Fe(CN)_6$ for 30 s.

Spectrophotometric and electrochemical studies was carried on the prepared electrode and its component to prove the role of each component in specific capacity and stability.

LRGO/Pani/PB film demonstrated excellent supercapacitor performance (401.8 F/g at 50 mV/s scan rate with 97.1 % capacitance retention for up to 1000 cycles) and (444.6 F/g at 1 A/g current density)

Three units connected in series of supercapacitor (each unit have two LRGO/Pani/PB electrodes) could light red and white LED light for more than 90 s

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