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Increasing Supercapacitor Features Using Reduced Graphene Oxide@Phosphorus

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Abstract: Supercapacitors have attracted much attention in the field of electrochemical energy storage. However, material preparation and stability limit their applications in many fields. Herein, a reduced graphene oxide@phosphorus (rGO@P) electrode was prepared using a simple inexpensive method. The new graphene structure (rGO@P) was characterized by X-ray diffraction, Fourier transform infrared spectroscopy, scanning electron microscopy and Energy-dispersive X-ray spectroscopy.

Electrode showed excellent performances (307 F g−1), which seem to be the highest among many other rGO@P-based electrodes reported so far. It also has an excellent cyclic stability up to 95% after 600 consecutive charge/discharge tests. So, the ease of the synthesis method and excellent performance of the prepared electrode materials mat have significant potential for energy storage applications.

Keywords: Reduced Graphene Oxide, Supercapacitor, Electrode, Phosphorous Functionalization

1. INTRODUCTION

In recent years, the use of portable electronic devices, including smart phones and laptops, has been considered a desirable approach to the advancement of human life [1], [2]. However, an increasing world population and an increasing demand for essential needs may lead to a future energy crisis [3], [4]. To overcome such a challenge, many studies have been conducted to develop novel energy storage devices, including lithium ion batteries, sodium ion batteries, and supercapacitors [5-7]. Supercapacitors are very promising candidates for future energy storage technology. Since there is no chemical reaction involved

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during charge storage in a supercapacitor based on electrochemical double-layer capacitance, stable operation exceeding one hundred thousand cycles is expected [9]. The intrinsic properties associated with typical supercapacitors are high power capabilities, fast charge propagation, charge-discharge process occurring within seconds, long cyclic life, low maintenance, and low self-discharging [10]. As a result, significant interest has developed around the field of energy storage in supercapacitors and supercapacitor-battery hybrid devices with research focusing on the development of novel materials that could beneficial increase the efficiency of these devices [11].

Nowadays graphene-based materials have been extensively studied because graphene is suitable for an active material in supercapacitors due to its large surface area and high electrical conductivity [12], [13]. However, the practical capacitive behavior of pure graphene is lower than the anticipated value due to the serious agglomeration during both the preparation and application processes [14]. Therefore, boosting the overall electrochemical performance of graphene-based materials remains a great challenge. As a result, solutions that are more exotic are frequently investigated, and given the additional step required in the manufacturing process to produce graphene from its oxidized counterpart there is increased interest in utilizing GO in energy storage applications [12]. The surface chemistry of electrode materials also plays an important role in their performance. Hence, the incorporation of heteroatoms into the carbon surface/lattice can modify the electronic properties of carbon materials, improving

their electronic conductivity and at the same time promoting the generation of functional groups that may undergo fast redox reactions, thus providing a pseudocapacitive contribution to the overall capacitance. The functionalization of carbon materials with several heteroatoms (oxygen, nitrogen [15], boron [16], or sulfur [17] has been extensively explored but scarce

reports are available on phosphorus-functionalized carbon materials, which calls for future research on this heteroatom. Phosphorus rich carbons have also been demonstrated to increase the capacitance due to pseudocapacitive processes, even if the mechanisms behind this behavior are not completely understood yet [18].

However, only a few studies are reported so far regarding graphene modified with phosphorus (P) and phosphorus-oxide (–POx) in electrochemical energy storage field. Recently, Karthika et al. prepared a high electrochemical activity P-doped graphene by reducing graphene oxide with phosphoric acid. The prepared sample exhibited a specific discharge capacitance value of 367 F g^{-1}, which is much larger than that of graphene [18]. This study suggests that the electrochemical properties of graphene can be effectively improved by introducing P into graphene. Therefore, it is very necessary to study the preparation and electrochemical properties of P and P–O group modified graphene. In addition, it was revealed that P-modified graphene was much more stable in air than N-modified graphene and exhibited improved n-type semiconducting behavior [19]. However, the traditional preparation methods are relatively complex and time-consuming. Wang et al. synthesized P/C hybrid through a simple ball-milling approach under argon protection. The whole preparation time was 16 h [20]. Xu et al. prepared P doped graphene via thermally annealing approach and the preparation time was more than 48 h [21]. To overcome these draw backs, it is necessary to use another fast and efficiency method to prepare P modified graphene material.

A new supercapacitor with the p-bearing groups deposited on graphene oxide surface as electrode was introduced in the present study to improve capacitance. The reaction between strong acidic groups such as phosphonate and the carboxylic groups GO bring about high activity and stability of the GO-based nanocomposites. Here, GO was functionalized with a simultaneous reduction to produce phosphonated rGO. So in this work PCl_3 as phosphorus resource was used to deposited P or P-O groups on graphene oxide surface.

The main intention of this research was to enhance the electroactivity of GO and increase capacitance properties. Introduction of Phosphonic compounds to GO nanosheets structures could be a promising approach to obtain an efficient and powerful electrochemical supercapacitor.

2. EXPRIMENTAL

A. Materials

The high purity of all used materials in this experiment were confirmed. The stock solutions were prepared by DDW (double distilled deionized water). Merck and Sigma-Aldrich Co provided us with the materials. The list of materials contained hydrogen peroxide (H_2O_2, 30%), Sulfuric acid (H_2SO_4), potassium permanganate ($KMnO_4$), sodium nitrate ($NaNO_3$), graphite powder (2000 mesh), Phosphorus trichloride (PCl_3).

B. Instruments

For electrochemical analysis, an Auto lab potentiostat/galvanostat (PGSTAT 302N) equipment with the NOVA 2.1 software was utilized. A usual three-electrode cell consisting of a reference electrode (Ag/AgCl/KCl (saturated)), a counter electrode (platinum rods), and a working electrode made of the synthesized nanocomposite was employed. With the help of an X-ray diffraction analysis (XRD, Model D8-Advance Bruner), FT-IR spectra (JASCO, 680 Plus), and field emission scanning electron microscopy (PHILLIPS XL30) coupled with energy-dispersive X-ray spectroscopy (EDX) techniques, the structural characterization of the developed nanocomposite was performed.

C. Synthesizing Graphene Oxide

The modified Hummer method [22] helped synthesizing. In a nutshell, 500 mL solution of concentrated H_2SO_4 (98%) heated to 80°C. Then, 10 g of graphite powder was added to the solution and it was stirred at 80°C for 120 min. The mixture was left to cool down at ambient temperature under stirring for one day. Hereafter, it was placed in an ice bath. Under constant stirring of the mixture, first 30 g $NaNO_3$ was added and then after 15 min, 30 g $KMnO_4$ was added gradually during cooling. Afterwards, for 2 h the stirring process was done at 20°C and again the stirring continued for one day in 25°C. During this time, color alteration from black to brown became apparent. Next the dilution process was carried out gradually using 200 mL of water and 1 h stirring. Immediately after using 600 mL of water to dilute the mixture, 150 mL of H_2O_2 was added to help elimination of any excess MnO_4^-, and the color alteration from brown to orange became apparent. Eventually, after filtering the mixture, it was washed with diluted HCl aqueous solution (1 L) to eliminate metal ions. Then, 1 L of DI water was utilized to wash the final product (GO) and remove the acid. Ultimately the resulting product was dried at 80°C.

D. Synthesizing and Preparing Modified Graphene (rGO@P)

To modified GO by Phosphorous or P-O functional groups a suspension of 5g of graphene oxide in 10 mL of Dry THF (Tetrahydrafuran) was inserted in reflux and then added 5 mL of PCl_3. Further, the solution was refluxed in an oil bath for 24 h at 80°C. Furthermore, resultant was separated through centrifuging, washed by using dry chloroform and hydrolyzed in water.

Eventually the synthesized composition was separated from solution through centrifuging, washed, using double distilled water and dried in oven at 70 °C.

The new synthesized composite was identified by using scanning electron microscopy (SEM) and X-ray diffraction, EDX and FT-infrared spectroscopy (FT-IR).

E. Preparation of Modified Glassy Carbon Electrode (GCE)

Glassy carbon as working electrode was polished by 0.050 μm alumina powder for 5min and washed by using water/ethanol solution in ultrasound bath for 5min in order to clean electrode surface. Then, to obtain homogeneous suspension of rGO@P, 10 mg of new synthesized nanocomposites was added to a 10 mL vial containing 1 ml water. The mixture was sonicated for 30 min in ultrasonic bath. In order to prepare electrode a 7.5 μL drop of prepared suspension was placed in the surface of glassy carbon electrode and dried at room temperature for 30 min.

Next, on the surface of the GCE, 7.5 μL of the rGO@P nanocomposite suspension spread out and left aside to let the solvent evaporate.

3. RESULTS AND DISCUSSION

Pseudocapacitive materials (phosphonate groups) were introduced to electric double layer GO after covalently grafted phosphonate functionalized groups on the surface of GO nanosheets.

At the end of phosphorous modified GO procedure, all of the P−Cl bonds of GO-PClx were converted to P−OH covalent bonds (scheme 1).

Additionally, in this study, a novel, safe, inexpensive and eco-friendly method to create high-quality graphene oxide nanosheets for energy storage was presented. In the new synthesized rGO@P, electrolytes have better access to more pores since the stacking issue was hindered.

A. Characterization of GO and rGO@P Derivatives

In FT-IR spectroscopy, the formation of covalent bonds can be confirmed according to the bonding energy and vibration modes of the covalently bonded atoms. The existence of oxygen functional groups on GO, the formation of P=O, C−O−P, P−O−P, and P−O−H covalent bonds in RGO@P, were affirmed by FT-IR spectra. Fig. 1A illustrates the FT-IR spectrum of the prepared graphene oxide. The main absorption peaks observed can be associated to the stretching vibrations of O-H (3399 cm^{-1}), C=O (1724 cm^{-1}) and bending vibrations of C-O (1170 cm^{-1}) and C-O-C (1050 cm^{-1}) which is evidently comparable with the previous reports. The phosphate functional group has an obvious PO−H stretching peak that appears at around 2900−3000 cm^{-1}. As is shown in Figure 1B, rGO@P has a strong witness peak around these wavenumbers (peak at 2924 cm^{-1}). Also, the P=O and P−O bonds appear at around 1200−1400 and 1000−1200 cm^{-1}, respectively, which depend on the substituents of phosphorus. These ranges of wavenumbers can overlap with the witnesses' peaks of GO, so the P=O and P−O bonds cannot be clearly specified. These peaks appear in Fig. 1 B at around 1128 and 1008 cm^{-1}. Both spectra show peak at around 1600 cm^{-1} (Fig.1 A 1600.7 cm^{-1} and in Fig. 1 B 1575 cm^{-1} correspond to C=C vibrations in graphene plane.

The disappearance of bands ascribed to -COOH groups (peak at 1724 cm^{-1}) is an additional piece of evidence of successful conversion of the carboxylic groups into phosphonic ones. The FT-IR functional groups peaks of Figure 1 are summarized in Table 1.

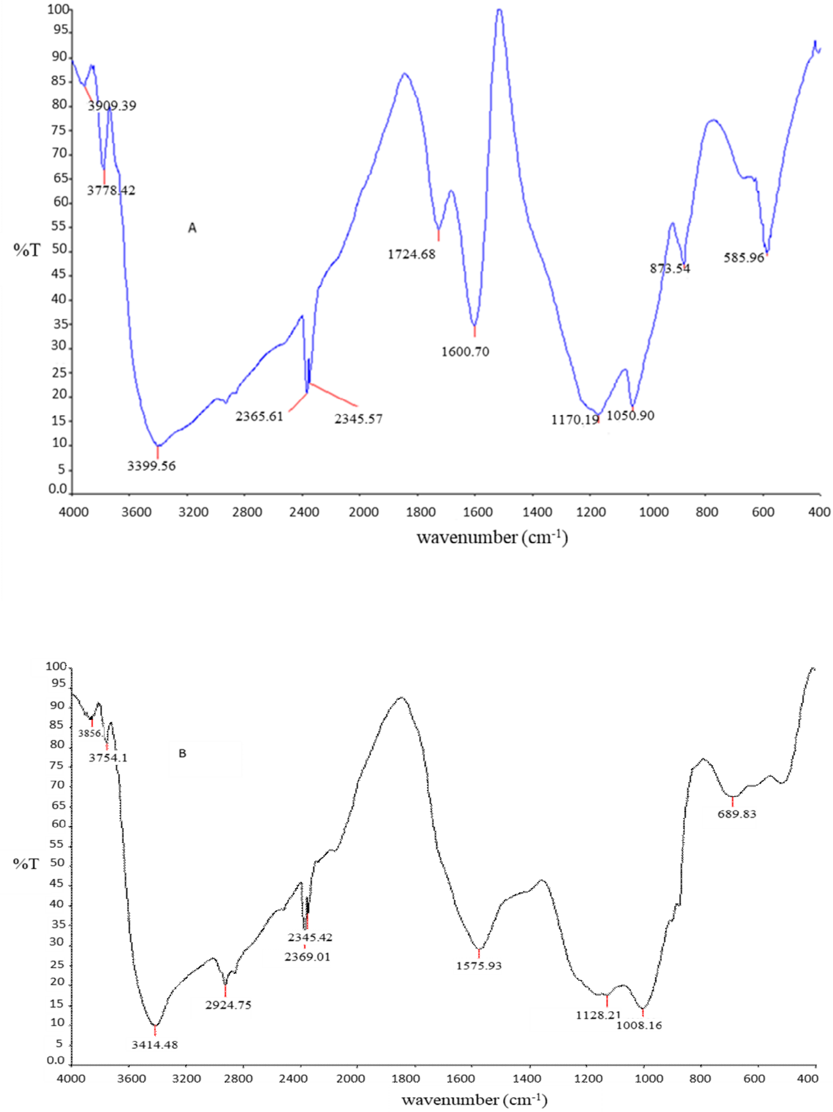


Fig. 1. FT-IR spectra of (A) GO and (B) rGO@P

TABLE 1. FT-IR Functional Groups Peaks from Figure 1

Wave number (λ) (cm^{-1})	Functional groups
Fig 1 (a)	
3399	O-H
1724	C=O
1170	C-O
1050	C-O-C
Fig 1 (b)	
2900−3000	PO−H stretching peak
1200−1400	P=O
1000−1200	P−O
1600.7	C=C

With the help of FESEM and EDX methods, the morphology and surface structural properties of GO, rGO@P were examined. In Fig. 2 A, the formation of thin layers of GO nanosheets with a few wrinkles on the surface is demonstrated. The SEM images of rGO@P nanoparticles (as shown in Fig. 2 B and C) disclose structural properties which are dissimilar to those of GO. Asymmetrical shapes with a multi-layered structure and surface wrinkles owing to crumpling, scrolling, and random aggregation to form disordered solids are demonstrated. Otherwise stated, the surface morphological alteration of phosphorous functionalized graphene in an identifiable way from that of GO was proven as the increments of number of wrinkles on the surface and multi-layered structure was clarified. The conversion of oxygen-containing carbon to a phosphorylated carbon caused disorderness in the basal plane. The decorated GO with Phosphorous groups (scheme 1) provides open channels and more porous structure with larger pore sizes for the access of electrolyte and ions, so higher energy storage capacity and minimize volume changes of phosphorous during discharge-charge processes were reported.

The EDX technique was used for the characterization of the GO, rGO@P (Fig. 3 and Table. 2). The presence of carbon and oxygen and the absence of other elements in GO suggests that the synthesized GO is pure (The data is consistent with previously reported data [23]). Elemental analysis shows that the rGO@P contain C, O, P and Cl elements and therefore the formation of the structure is proven. The presence of a high amount of P in the synthesized rGO@P suggests successful synthesis of nanocomposite.

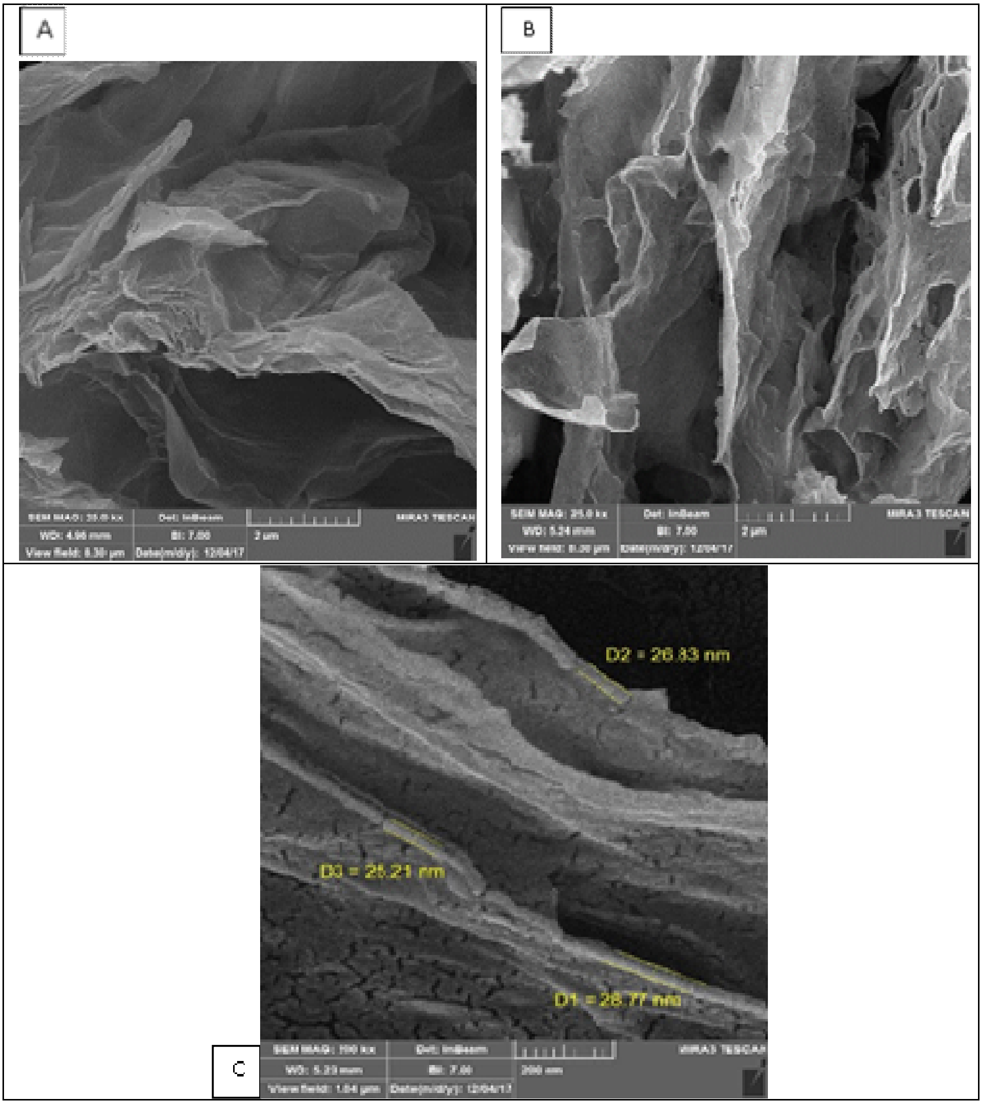


Fig. 2. SEM image of (A) GO, (B, C) rGO@P

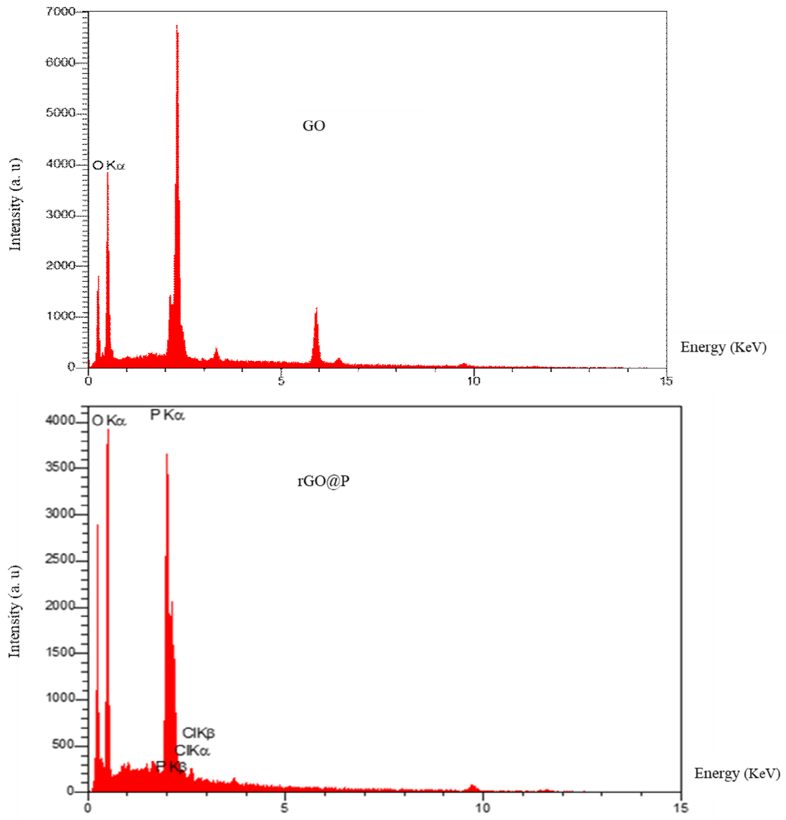


Fig. 3. EDX of GO and rGO@P

TABLE 2. EDX analysis of GO and rGO@P

	GO	rGO@P
Elements	%W	%W
C	61.46	35.63
O	38.54	42.09
Cl	--	1.71
P	--	20.57
	100.00	100.00

The phase composition of GO is characterized using XRD (Fig. 4). The sharp peak centered at 11.7° is ascribable to (001) reflection peak. rGO shows two peaks: one small peak centered at 2θ = 11.7° and another broad peak at 2θ = 25.8°, corresponding to interlayer distances of 4.47 and 3.53 Å, respectively. These XRD results are related to the exfoliation and reduction processes of GO and the processes of removing intercalated water molecules and the oxide groups.

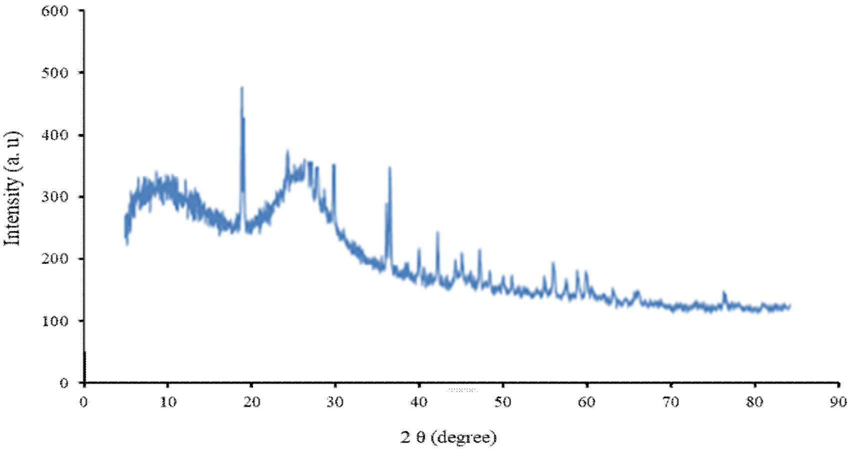
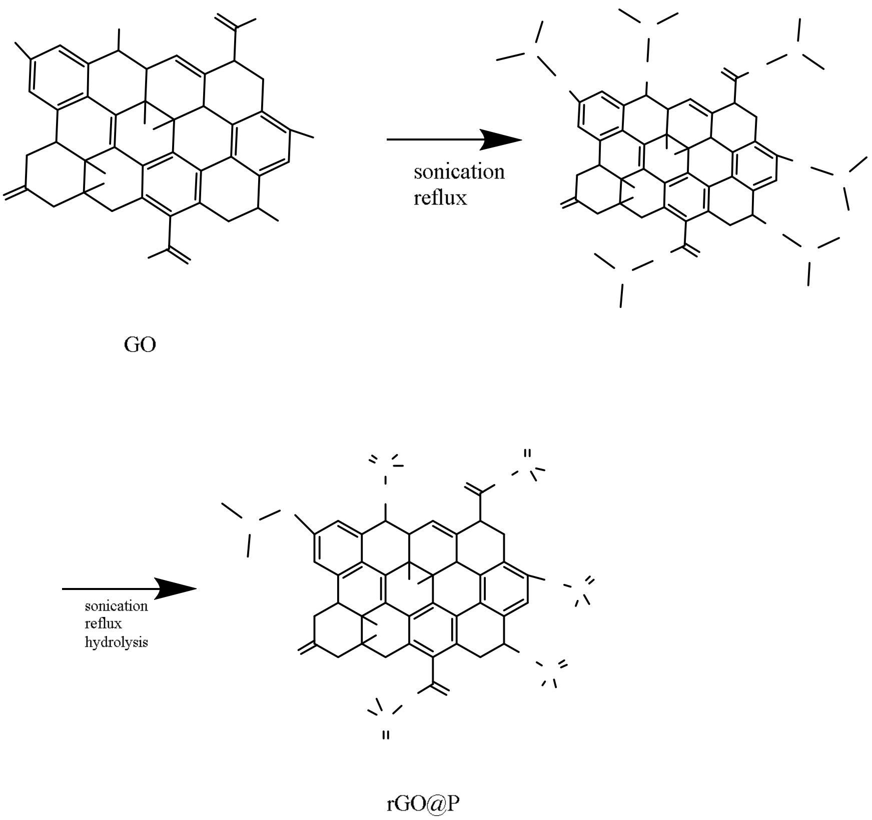


Fig. 4. XRD pattern of rGO

The typical procedure for phosphorylation of GO is summarized in Scheme 1. The preparation of Graphene oxide nanosheets (GO) was done employing a modified Hummer's method, and was subsequently functionalized with PCl3 as phosphorus reagents of the phosphorylation reaction. PCl3 as chlorine phosphorus reagent (PClx) shows high reactivity in a substitution reaction. Afterward, the mixture was refluxed for 24 h at 80 °C. It was cooled to room temperature, poured cautiously into DI water, and hydrolyzed. At the end of this step, all of the P−Cl bonds of GO-PClx were converted to P−OH covalent bonds. At the end of this step, all of the P−Cl bonds of GO-PClx were converted to P−OH covalent bonds.



Scheme. 1 Preparation Route and Structure Model of rGO@P

B. Electrochemical Characterizations of rGO@P Nanocomposite

To examine the electrochemical behaviors of the nanocomposite for supercapacitor applications the galvanostatic charge-discharge (GCD) and cyclic voltammetry (CV) methods were used [7]. All the procedures were carried out in a three-electrode cell containing 1 mol L^{-1} H_2SO_4 electrolyte. Firstly, for the pre-treatment of prepared working GCE, CV technique was employed. CV cycles were applied in the range of (-0.6 to 1.0 mV) until stable voltammograms were procured. As evident in Fig 5, stable voltammogram was procurable after 50 cycles.

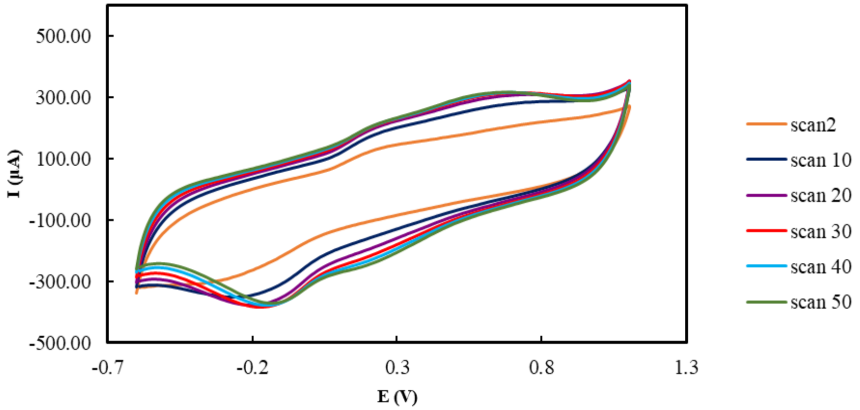


Fig. 5. CV curves of rGO@P at different scan numbers at scan rate 10 mV s^{-1}

At the start, the electro-activity of GO, rGO@P nanocomposite was studied by CV method at the scan rate of 10 mV s^{-1}. Fig. 6 shows that the insulating characteristics of GO results to a quite low current response which is negligible compared to rGO@P. The CV of rGO@P displays a practically rectangular frame carrying the redox peaks which show a relatively pseudocapacitive behavior [12]. The almost rectangular appearance of CV plot attributes to the electrical double layer capacitance (EDLC) feature of rGO@P.

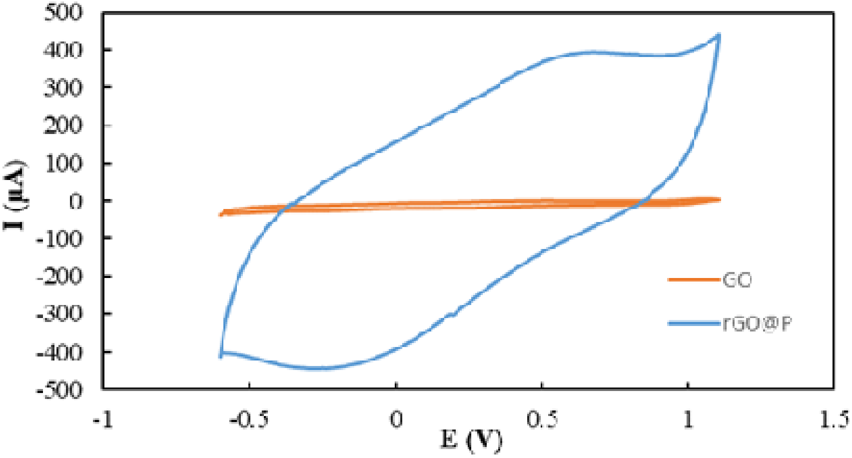


Fig. 6. CV curves of GO and rGO@P at scan rate 10 mV s^{-1}

GCD method was applied to determine the specific capacitance of prepared electrodes using Eq. 1:

$C = I\,\boldsymbol{\Delta}t/m\,\boldsymbol{\Delta}V$ s (1)

where I is the current (A), Δt is the discharging time (s), m is the amount of nanocomposite (g) and ΔV is the potential window (V). According to Fig. 7 the charge/discharge specific capacitance of GO (2.54 F g−1) at a current density of 1 A g−1 is almost negligible compared to rGO@P (307 F g−1). This behavior can due to that these nanomaterials have a wide range of porous structures. Probably, these porous structures were formed by crinkling of the accumulated sheets.

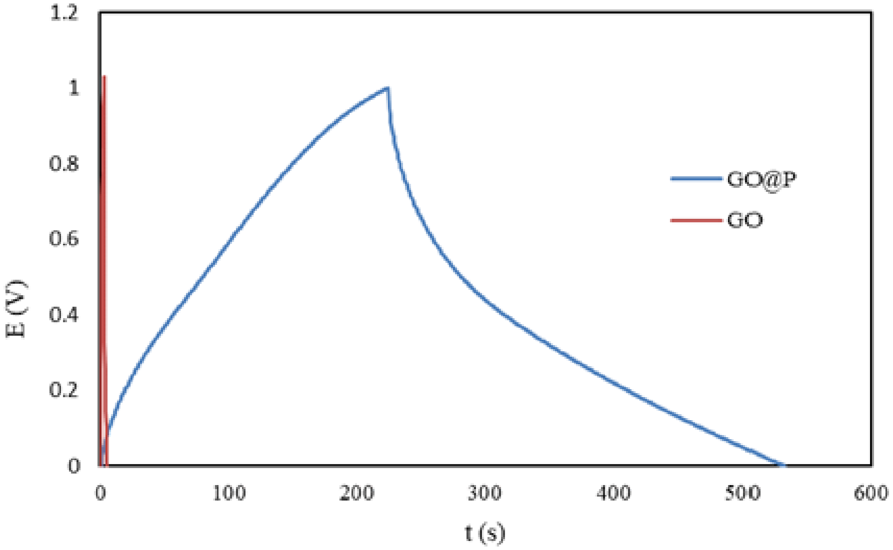


Fig. 7. GCD plots of GO, rGO@P at the current density of 1 A g^{-1}

For further evaluation, the GCD curve of nanocomposite at the current densities of 1, 2, 3, 4, 7 and 10 A g^{-1} was procured (Fig. 8) and utilized to extract the specific capacitance in each case. Then after a thorough investigation was performed on the impact of current density on specific capacitance (Fig. 9). As shown in Fig. 9, any increase in the current density results in a decrease in the specific capacitance which holds true for supercapacitors and is mostly encouraged by the diffusion limitation of electrolyte ions in the micro pores of the electrode.

Based on Fig. 9, the possibility of retaining roughly 42 % capacitance by rGO@P nanocomposite is not far-fetched especially when current density is increased by 10 times. This potentiality confirms that rGO@P has remarkable electron and ionic migration performance.

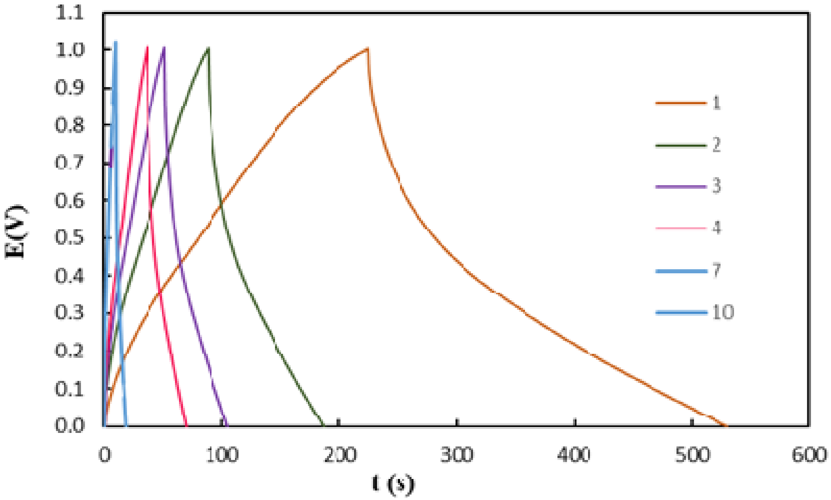


Fig. 8. The charge-discharge diagram (GCD) of rGO@P at different current density in A g-1 unit

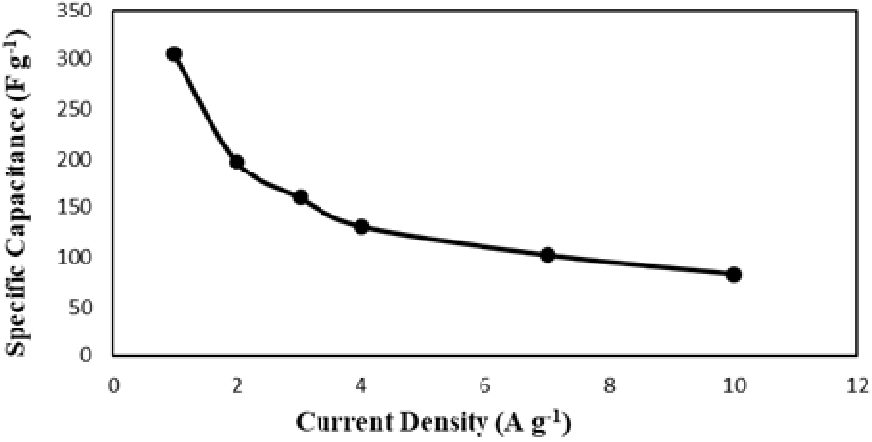


Fig. 9. The specific capacitance of rGO@P electrode versus the current density calculated from Fig. 8

In Fig. 10, the cyclic voltamograms of the rGO@P at diverse scan rates ranging from 1 to 70 mV s^{-1} is demonstrated and shows that the current of modified GCE electrode boosts as the scan rate is increased however, the anodic to cathodic peak current ratios stay more or less constant for all scan rates showing a quasi-reversible behavior.

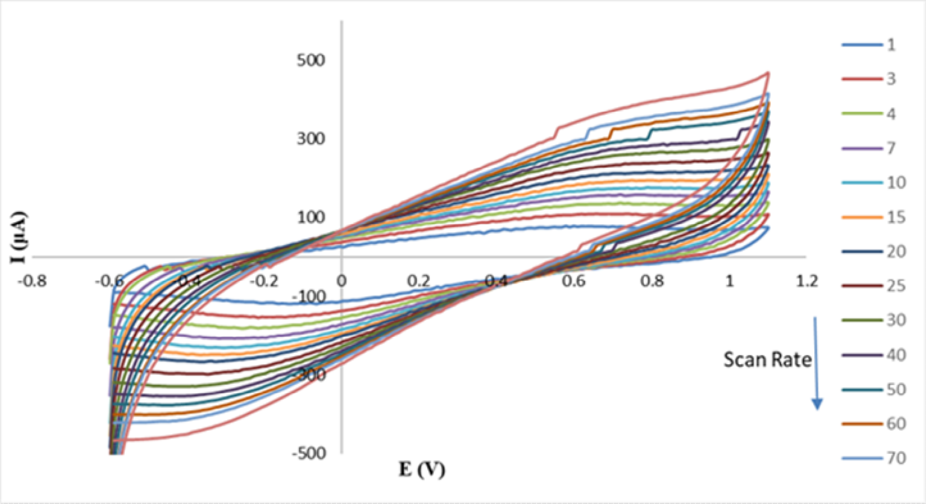


Fig. 10. CV of rGO@P at different scan rates in mV s^{-1} unit

The GCD was collected for 600 cycles at the current density of 30 A g^{-1} to check the optimized electrode durability and stability. Based on the information in Fig. 11, it became apparent that roughly 92% of the initial capacity was maintained.

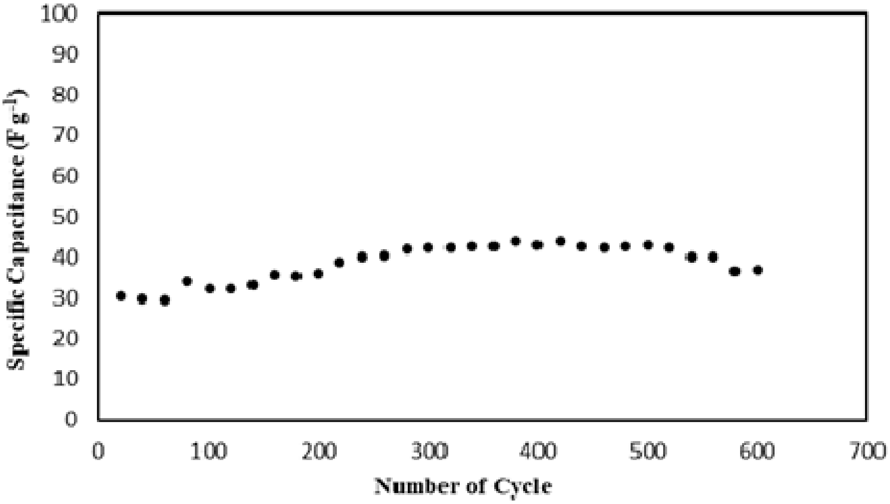


Fig. 11. The cycling stability of rGO@P at a current density of 30 A g^{-1}

In Table. 3 the results of some previous reports are compared to those of the present study. In conclusion it was demonstrated that the developed nanocomposite presents remarkable supercapacitive properties when compared to other studied ones.

TABLE. 3. Performance comparison of some reported studies and presented nanocomposite

Electrode composition	Electrolyte	Cell set up (Electrode)	Potential window (V)	Cyclic stability (%)	Specific capacitance (F g^{-1})	Current density (A g^{-1})	Ref.
ativated nitrogen doped graphene	1 M KOH	3	1.0	93.5% after 500 cycles	132.4	0.1	[24]
r GO functionalized 2,2-diaminopyridine cobalt complex	1M H2SO4	3	1	100 % after 500 cycles	107.0	1.0	[25]
polyamic acid (PAA) and polyvinyl pyrrolidone (PVP) blends electrospun fiber	ionic liquids electrolyte	3	3.4	1000 cycle	211.7	0.1	[26]
activation of carbonized cellulose cloth	30% KOH	2			170		
reduced graphene oxide/polyaniline/polyvinyl alcohol	1.0 mol/l HCl	3	1.4		174	0.0015 mg scan rate 50 mV s^{-1}	[27]
oxygen/sulfur/nonoporous carbon	in 6 M KOH	3	1	5000 92.34 %	168	1	[28]
leavening agent-rGO	3.0 M KCl	2	1	5000 80%	112.1	0.1	[29]
This work	1.0 M H_2SO_4	3	1	600 92%	307	1	

4. CONCLUSION

In the current article, an uncomplicated low-cost method has been introduced to synthesize rGO@P as a Phosphorous functionalized electrode material for hybrid supercapacitance utilizations. For the structural characterizations, different techniques namely FTIR, FESEM, EDX, and XRD were employed. The results confirmed that the Phosphorous containing functional groups were successfully introduced into GO by covalently grafting rGO@P onto GO nanosheets. This positioning could improve the nanocomposite charge transfer and capacitance.

The nanocomposite exhibits the specific capacitance of 307.0 F g^{-1} at a current density of 1 A g^{-1} which is in the higher value juxtaposed to individual Go nanosheets. Adding Phosphorous to GO nanosheets provided bigger surface area, more porosity with enhanced conductivity as a result of disorderness in the basal plane in the nanocomposite.

In addition, the rGO@P displayed up to 92% capacitance retention after 600 GCD cycles suggesting favorable cyclic stability which was explainable by the binding impact of Phosphorous functional groups. In essence, after doing a thorough investigation, it has been assumed that the introduced nonocomposite has excellent potentialities to be utilized for supercapacitance applications.

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