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Original scientific paper

Synthesis of graphene by electrochemical exfoliation from petroleum coke for electrochemical energy storage application

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Abstract

The objective of the present work was to synthesize a graphene-like structure from petroleum coke (pet coke). Graphene is a potential alternative conducting material to replace traditional electrode materials such as indium tin oxide. The phosphoric acid was used to activate the pet coke in conditions where the coke to acid ratio is varied as 1:1, 1:2, 1:3, 1:4 and 1:5. The samples were kept at different temperatures in the furnace maintained in inert atmospheric conditions at 400, 500 and 600 °C for activation time intervals of 1, 2 and 3 h. The extent of activation of pet coke samples was characterized by their yield and iodine number. For the optimized conditions (600 °C, 3 h, 1:4 coke to acid ratio), the activated pet coke was moulded and taken as the anode for electrochemical exfoliation using platinum wire as cathode, and 0.3 M H_2SO_4 *solution as electrolyte. The electrochemical exfoliation was carried out using DC power supply at 22 V for 8 h, and the obtained exfoliated product was analysed by surface-sensitive techniques (XRD, Raman and SEM). The specific capacitance values were measured using cyclic voltammetry in KOH,* Na_2SO_4 *and* H_2SO_4 *electrolytes. The highest specific capacitance value of 40 F* g^{-1} *for the scanning rate of 25 mV* s^{-1} *was obtained in 1 M* H_2SO_4*. It was confirmed that graphene-like structure produced from activated pet coke can be used as an alternate material for supercapacitor applications.*

Keywords
Chemical activation; graphene like structure; supercapacitor

Introduction

Petroleum coke is a carbonaceous by-product obtained in large amounts in the crude refining process. It is abbreviated as coke or pet coke and is rich in carbon content. Petroleum coke has limited applications, except for direct replacement of fuel in combustion, which is due to its high calorific value >32.635 MJ kg^{-1} (7800 kcal kg^{-1}), compared to 14.644 to 18.828 MJ kg^{-1} (3500 to

4500 kcal kg^{-1}) [1]. Generally, petroleum coke could have many applications, such as supercapacitors for electrochemical energy storage applications, effective adsorbent material, and as an alternate for coking coals in the production of metallurgical coke [2-4].

Supercapacitor is an electrochemical energy storage device that attracts a lot of attention due to its higher power density, fast charge and discharge rate, and good stability [5,6]. Generally, porous forms of carbon materials have been used in supercapacitors as energy storage media because of their large surface area, favourable pore size distribution, high conductivity and chemical stability [7,8]. To prepare activated carbon material, various carbon-rich raw materials can be used, such as rice husk [9], bamboo [10], banana fibres [11], sugar cane bagasse [12], cassava peel waste [13], *etc*. Pet coke can also be used as a precursor for carbon and conversion to a graphene-like structure. Many authors studied and activated the petroleum coke with different activation techniques [14,15]. The activated coke is converted to a graphene-like structure. Graphene has a two-dimensional honeycomb sp^2 carbon lattice and exists in different forms, such as graphene oxide (GO) and reduced graphene oxides (RGO) [16]. These materials have many potential applications in the future, while currently, they are mostly used for biomedical applications [17] and energy storage devices [18] due to their excellent electrical, mechanical and chemical properties.

There are various techniques of graphene production, such as chemical vapour deposition, chemical exfoliation of graphite, liquid exfoliation of graphite crystal, microwave reduction, direct arc discharge, *etc*. [19]. Recently, attention was paid to the electrochemical exfoliation of graphite, which is easy, fast and eco-friendly technique to produce high-quality graphene [20]. Edison *et al.* [21] studied electrochemical exfoliation of graphite foils taken as both anode and cathode. Graphite was converted into graphene sheets in 0.1 M ammonium sulfate solution at the constant voltage of 10 V. The exfoliated graphene sheets were characterized and the specific capacitance of 84.82 F g^{-1} was determined by cyclic voltammetry at 2 mV s^{-1} scanning rate. The authors reported that graphene sheets act as a good material for supercapacitor in KOH electrolyte solution. Zhou *et al.* [22] reported the exfoliation of graphite cathode by electrochemical intercalation using Na^+/dimethyl sulfoxide complexes as an intercalation agent and thionin acetate to produce and stabilize few-layered graphene. Loudiki *et al*. [23] experimented to produce graphene from pencil graphite electrodes by electrochemical exfoliation technique using 11 V imposed between two pencil electrodes in the presence of 0.1 mol L^{-1} Na_2SO_4 aqueous solution. The authors observed that graphene oxide and reduced graphene oxide were produced. Roscher *et al*. [24] reported cathodic exfoliation of natural graphite flakes pressed at a boron-doped diamond electrode to produce single-layered to few-layer graphene at an applied negative potential of -60 V. The authors reported that a 70 % yield was obtained. Saha *et al.* [25] studied electrochemical exfoliation to produce graphene nanosheets from petroleum coke rather than graphite. The voltage of 12 V was applied, and the graphene sheets from different types of coke possessed increased electrical conductivity. In general, few authors attempted to produce graphene and graphene-like materials from petroleum coke.

Petroleum coke, which contains high carbon content, is generated abundantly as a residue from the refinery process industry. Therefore, in this work, an attempt was made to convert this waste residue into a valuable material for energy storage applications. For this purpose, the petroleum coke was first activated using chemical activation with phosphoric acid at different conditions and then electrochemically exfoliated to produce graphene materials tested for supercapacitor applications.

Experimental

Petroleum coke

Petroleum coke was collected from the refinery industry of Chennai Petroleum Corporation Limited, Chennai, India, which is a carbon residue left after distillation of petroleum. All the chemicals, such as phosphoric acid and sulfuric acid, were purchased from Sisco Research Laboratories Pvt. Ltd, India and used for experiments without further purification. Moisture, ash, volatile matter and fixed carbon contents of the pet coke were analyzed by typical proximate analysis techniques and the values are given in Table 1. The coke was crushed and the particles are sieved in the sieve shaker. An average particle size was measured as 150 μm.

Table 1. *Proximate analysis of petroleum coke*

Test	Content, wt.%
Moisture content	0.95
Ash content	0.32
Volatile matter	9.00
Fixed carbon	89.73

Chemical activation of petroleum coke

The petroleum coke sample of 3 g was activated by chemical activation using phosphoric acid. Pet coke and phosphoric acid were mixed in the ratio of 1:1 (1 g of coke and 1 g of 90 % H_3PO_4) 1:2, 1:3, 1:4, and 1:5, kept in the furnace and maintained in inert atmospheric condition at a temperature of 400, 500 and 600°C, respectively, during time intervals of 1, 2 and 3 h. The samples were allowed to cool to room temperature, washed repeatedly with distilled water to remove the excess of present chemicals, and dried in a hot air oven at 105 °C at a time interval of 2 h. The activation of petroleum coke was analyzed by yield percentage and iodine number. The yield of the activated pet coke samples is found from the equation (1):

$$\text{Yield} = \frac{\text{Weight of sample after activation}}{\text{Initial weight of sample}}100 \qquad (1)$$

The iodine number is measured using the standard procedure. 10 ml of 0.05 M iodine solution was taken in a conical flask, and two drops of 1 % starch solution were added. The pale yellow colour of the iodine solution turns blue. The solution was titrated with 25 mM sodium thiosulphate till it became colorless. Burette reading that corresponds to blank reading was noted as (B). Then 0.2 g of activated coke was taken in the iodine flask and 40 ml of 0.05 M iodine solution was added. The solution was shaken for 4 minutes prior to filtering. 10 ml of the filtrate was titrated against thiosulphate solution using starch as an indicator and the titrated value is noted as (A). The iodine number (mg g^{-1}) was determined by equation (2), and the activated pet coke was dried and stored in a desiccator.

$$\text{Iodine number} = \frac{\left(\text{B - A}\right) \times \text{molecular weight of iodine} \times \text{normality of iodine} \times 40}{\text{B} \times \text{weight of carbon}} \qquad (2)$$

Electrochemical exfoliation

Electrochemical exfoliation was performed in an electrolysis cell. The typical experimental setup and its lab photo are shown in Figure 1. The synthesized graphene is mixed with polyvinylidene fluoride (PVDF) as a binder at the weight ratio of 9:1, the weight ratio of 18 g of activated pet coke and 2 g of PVDF binder. The mixture was moulded in a mechanical press at 100 °C and 100×10^5 N m^{-2}

pressure. A sample of 10 cm in length and 15 mm in diameter of formed solid coke was taken as an anode and Pt wire as a cathode. The coke was connected with a wire and attached to the DC power supply, while the wire contact with the solution was protected by glue to avoid the connected wire dissolution during the reaction. This whole anode assembly was dipped into 0.3 M H_2SO_4 solution to immerse coke in the electrolyte fully. The electrochemical exfoliation was carried out by applying DC voltage ranging from 12 to 28 V for 8 h. The sample weight of 10 g per run was taken. After exfoliation, the sample was allowed to settle down in the cell and then the sample was filtered. The filtered samples were dried in a hot air oven at 80 °C for 1 hour and then analyzed.

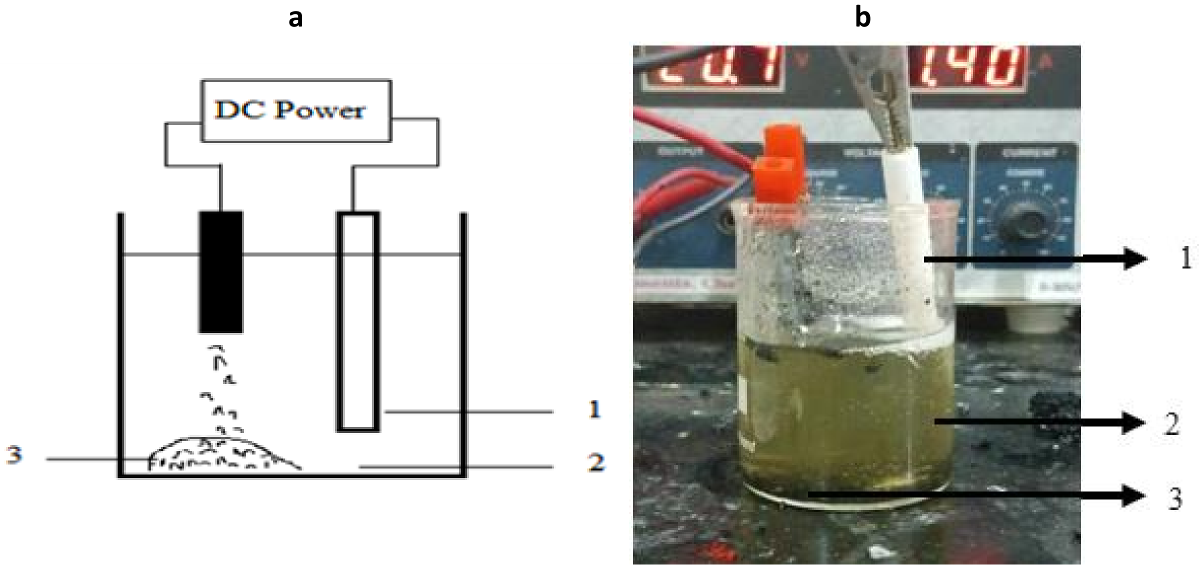

Figure 1. *Experimental setup of electrochemical exfoliation process: (a) schematic representation and (b) photo view of lab experiment, 1 -platinum wire electrode; 2 - electrolyte solution; 3 -graphene powder*

Cyclic voltammetry

An electrochemical workstation (Admiral Instruments, USA) was used for electrochemical studies in the present work. A conventional three-electrode system (working, counter and reference electrodes) consisted of a graphene sample as the working electrode, platinum wire as the counter electrode, and saturated calomel electrode (SCE) as the reference electrode. To prepare the working electrode, exfoliated graphene was dispersed in 150 mg of the sample containing 100 µL ethanol and mixed with 5 wt.% Nafion solution for 20 minutes. Then, 2.5 µL of the sample was coated on a glassy carbon electrode and dried. The supercapacitor property of materials was investigated in three different electrolytes: 1 M Na_2SO_4, 2 M KOH, and 1 M H_2SO_4. The cyclic voltammetry (CV) technique was used to characterize the material in a potential window of -0.2 to 0.2 V *vs.* SCE at 25, 50, 75, 100 and 125 mV s^{-1} scan rates.

Results and discussion

Activated petroleum coke

Activated petroleum coke yield and iodine number were experimentally determined for different activation temperatures (*t*): 400, 500 and 600 °C, different coke to phosphoric acid weight ratios: 1:1, 1:2, 1:3, 1:4, 1:5 and different activation times: 1, 2 and 3 h. The values of iodine number and activated petroleum coke yield are listed in Table 2.

Table 2. *Yield and iodine number of pet coke activated at different coke-to-phosphoric acid ratios, temperatures and activation times*

Time, h											
1				2				3			
Ratio*	t / °C	Yield, %	I number, mg g^{-1}	Ratio*	t / °C	Yield, %	I number, mg g^{-1}	Ratio*	t / °C	Yield, %	I number, mg g^{-1}
1:1	400	80	390	1:1	400	79	640	1:1	400	67	460
1:2	400	82	640	1:2	400	81	770	1:2	400	71	520
1:3	400	85	760	1:3	400	85	870	1:3	400	73	870
1:4	400	95	850	1:4	400	90	960	1:4	400	79	992
1.5	400	90	840	1:5	400	87	920	1:5	400	85	962
1;1	500	74	540	1:1	500	68	550	1:1	500	83	670
1:2	500	78	763	1:2	500	73	620	1:2	500	85	850
1:3	500	81	780	1:3	500	75	640	1:3	500	87	870
1:4	500	90	900	1:4	500	79	890	1:4	500	91	988
1:5	500	88	890	1:5	500	81	870	1:5	500	90	962
1:1	600	79	640	1:1	600	77	800	1:1	600	85	1190
1:2	600	83	890	1:2	600	80	920	1:2	600	88	1330
1:3	600	88	1190	1:3	600	82	1020	1:3	600	91	1360
1:4	600	92	1300	1:4	600	90	1500	**1:4**	**600**	**97**	**1900**
1:5	600	91	1220	1:5	600	86	1489	1:5	600	95	1800

*Coke to phosphoric acid weight ratio

The iodine number is an important parameter for energy storage applications because it provides insight into the materials' surface area, porosity, and ability to adsorb and desorb molecules. The iodine number is a measure of the microporosity and surface area of the activated carbon. Activated pet coke with high iodine number typically has a large surface area and micropores. High surface area and porosity can enhance the material's capacity to adsorb and store ions, an important supercapacitor property. Data in Table 2 show that the iodine number of activated petroleum coke increases with an increase in temperature, coke-to-phosphoric acid ratio and activation time. The iodine number of activated petroleum coke prepared with an activation temperature of 600 °C is higher than 400 and 500 °C for all ratios. This is due to more extensive volatile matter degradation at higher activation temperatures. For temperatures beyond 600 °C, there is no improvement in the activation property observed. The highest iodine number is obtained after 3 h of coke activation at the activation temperature of 600 °C and coke-to-acid ratio of 1:4 (Table 2), and just this particular sample of activated coke was used for further examinations.

FTIR analysis of activated petroleum coke

The effect of functionalization of the chemical structure of petroleum coke with respect to its molecular interactions can be inferred from Fourier transform infrared spectroscopy (FTIR). The FTIR spectrum of the highly activated coke sample at a time interval of 3 h at 600 °C for the activation ratio of 1:4 is shown in Figure 2. In the FTIR spectrum, a bond stretching is manifested at 1740 cm^{-1} due to the vibration of C=O bonds. The presence of this stretching is sharp, indicating the presence of a large number of C=O bonds. This increase may be due to the presence of functional groups in phosphoric acid indicating successful grafting of acid onto the surface of coke. A C-N bond stretching can be seen at 1217 cm^{-1} due to stretching amine functional groups in pet coke. The stretching at 1367 cm^{-1} is due to the presence of hydroxyl functional groups. The intensity of -OH functional groups is sharp, depicting the presence of excessive hydroxyl ions. This occurs due to the presence of -OH groups in phosphoric acid, leading to excess hydroxyl ions in the system. The successful grafting and presence of phosphoric acid on the surface of pet coke can be confirmed by the FTIR spectrum, indicating a strong molecular interaction between them.

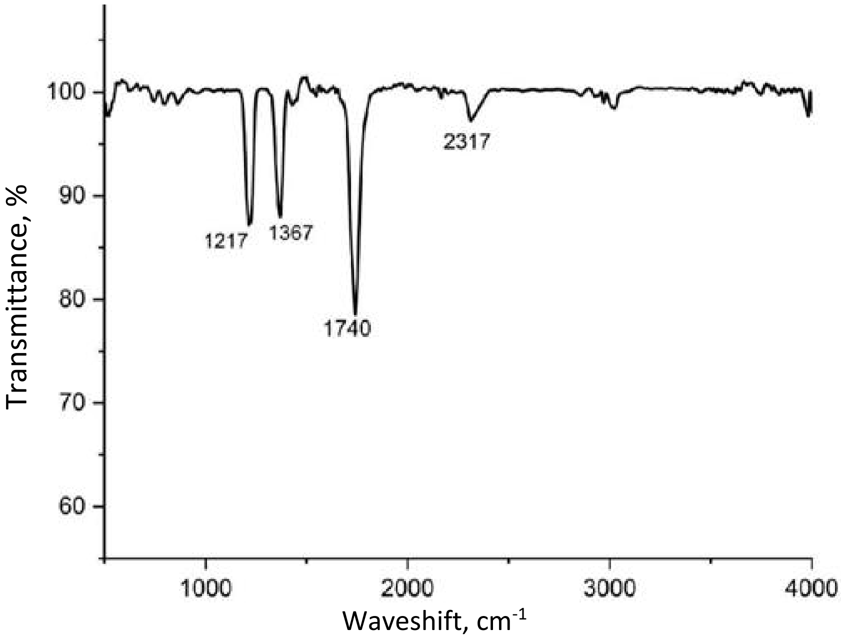

Figure 2. *FTIR spectrum of pet coke activated at coke to phosphoric acid weight ratio 1:4; activation temperature 600 °C; activation time 3 h*

SEM image of activated pet coke

Scanning electron microscope (SEM) micrograph of the same activated pet coke sample is shown in Figure 3. Phosphoric acid used for pet coke treatment leads to an increase in pore structures. The phosphoric acid acts as a catalyst on the surface of pet coke and along its ridges, which proves the covalent functionalization of phosphoric acid on the surface, thereby ensuring activation of coke.

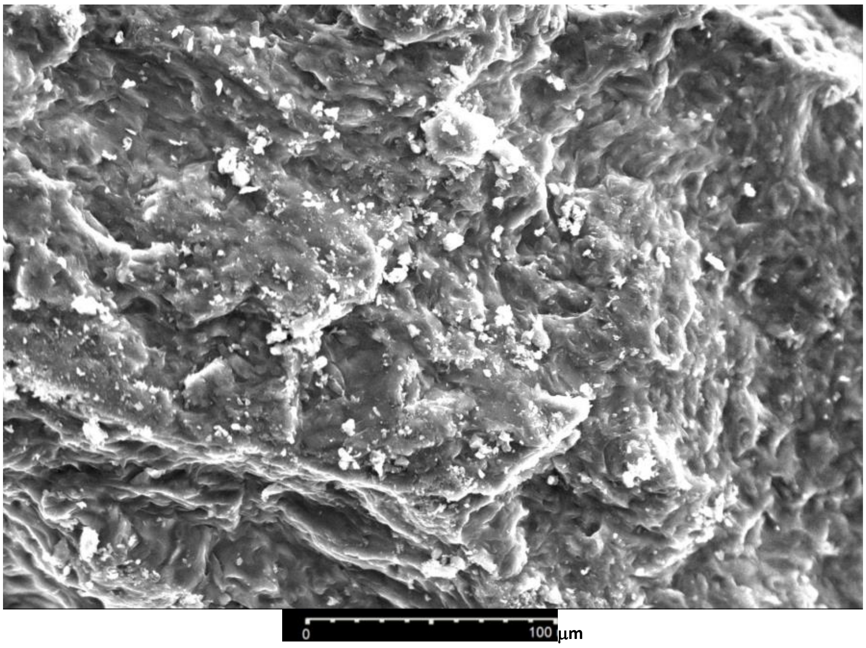

Figure 3. *SEM image of pet coke activated at coke to phosphoric acid weight ratio 1:4, activation temperature 600 °C, and activation time 3 h*

Effect of operating parameters on electrochemical exfoliation

The effects of different operating parameters, such as time, voltage and concentration of H_2SO_4 electrolyte, on the yield of the graphene are shown in Figure 4. The effect of exfoliation time is shown in Figure 4a. It is observed that the increase of exfoliation time continuously increases the yield of graphene, which may be due to more exfoliation occurring during longer exfoliation time. The applied voltage varied from 12 to 28 V of DC power source and the graphene yield after 8 h of exfoliation is shown in Figure 4b. The highest yield occurs at 22 V, while the further increase of the voltage reduces the yield of the graphene. For the applied voltage of 22 V for 8 h, a yield of 59.62 % graphene was obtained, while at either higher or lower voltages, lower yields were obtained. The very low graphene yield obtained for a voltage of 12 V is probably due to inadequate current density to initiate the exfoliation process. At the voltage of 28 V, however, a lower yield is obtained because higher voltage causes agitation, which causes the coke particles to fall off into large non-exfoliated particles, resulting in a lower yield. The results showed that high potential applied on pet coke would increase the yield of graphene, but the quality of graphene becomes lower with higher defects under high potentials. Sulfuric acid is widely used as an electrolyte for the electrochemical exfoliation of graphite to get graphene-like material because SO_4^{2-} ions in the acid relatively easily intercalate into graphite, resulting in fast exfoliation of coke material.

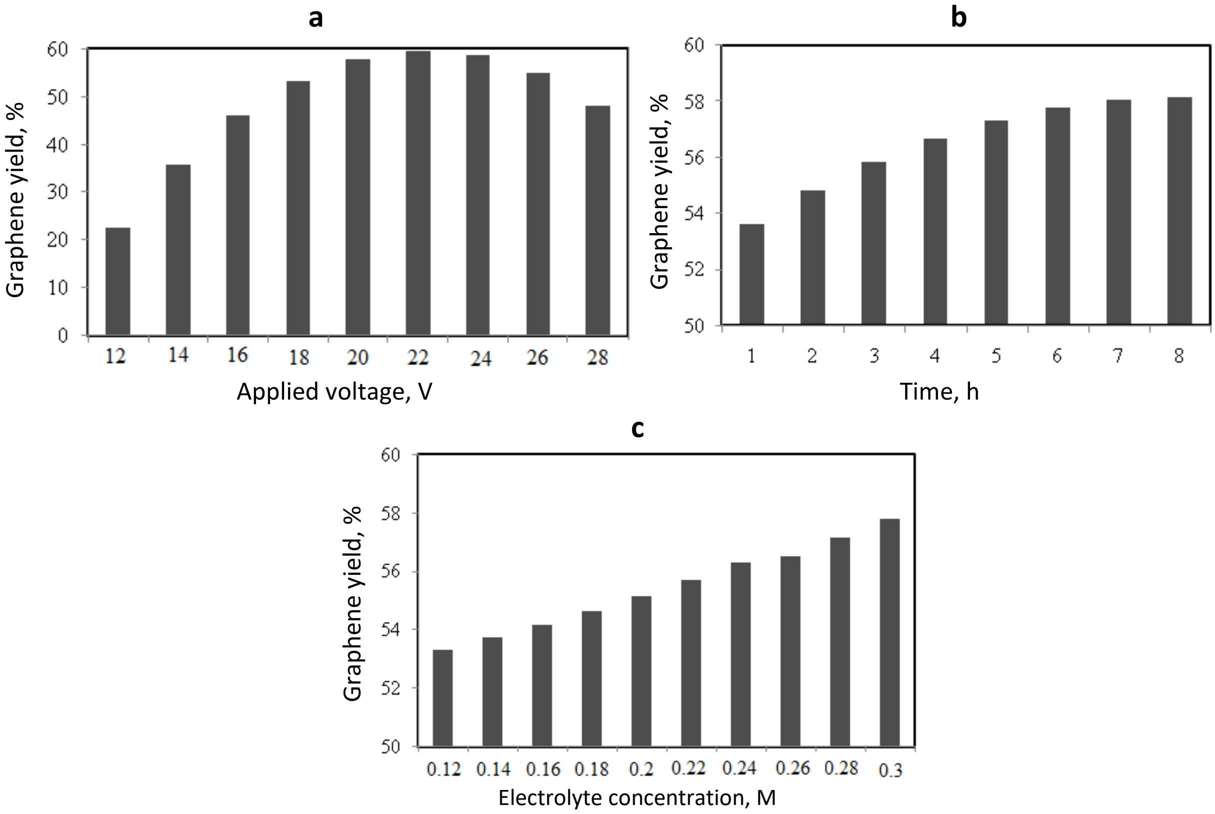

Figure 4. *Effect of different operating parameters on electrochemically exfoliated graphene yield: (a) effect of time for voltage 20 V and electrolyte concentration 0.3 M* H_2SO_4*; (b) effect of voltage for time 8 h and electrolyte concentration 0.3 M* H_2SO_4*; (c) effect of* H_2SO_4 *electrolyte concentration for time 8 h and voltage 20 V*

XRD analysis of exfoliated graphene-like structure

A wide-angle XRD characterization was done to determine the arrangement and crystallinity of the graphene oxide structure and results are shown in Figure 5. The XRD spectrum, measured in the range of 2θ from 5 to 100°, showed a diffraction peak ~10.2°), indicating a normal GO peak as seen in a previous study [26]. Bragg's equation was applied to find the interlayer spacing (*d*), resulting in a value of 0.89 nm. The disappearance of the peak at 25° proves that the exfoliation of the anode results in the formation of oxygen-containing functional groups. An increased interlayer distance between consecutive carbon basal planes is attributed to the intercalation of oxygen functional groups and water molecules into the carbon layer structure.

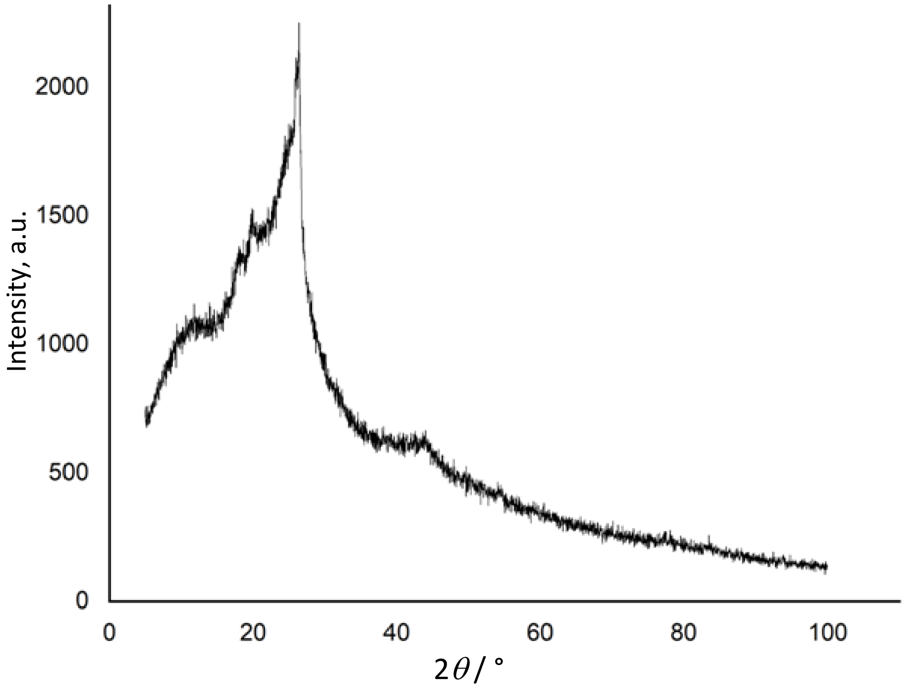

***Figure 5**. XRD result of electrochemically exfoliated graphene oxide. Electrolyte concentration: 0.3 M H_2SO_4; applied voltage 22 V; electrochemical exfoliation time: 8 h*

Raman spectroscopy of exfoliated graphene-like structure

Raman spectroscopy is an efficient method to provide information about interactions, especially electron-phonon interactions in carbon-based nanomaterials. Raman spectrum gives information about electron-phonon interaction (G band), defects present in hexagonal structure (D band) and fingerprint region (2D region) [27]. The Raman spectrum of powder GO shown in Figure 6 displays two important peaks at 1414.9 and 1663.5 cm^{-1}, related to the well-documented D and G-bands.

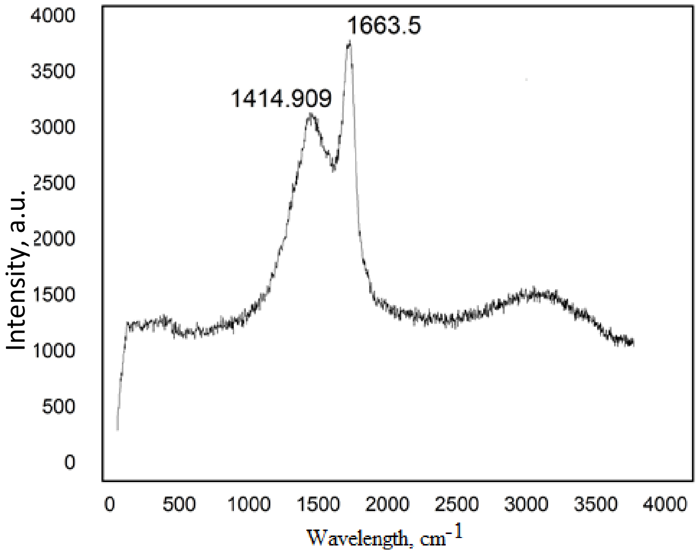

***Figure 6**. Raman spectrum of electrochemically exfoliated graphene oxide.*
Electrolyte concentration: 0.3 M H_2SO_4; applied voltage: 22 V; electrochemical exfoliation time: 8 h

Generally, graphene oxide synthesized by the chemical method has a strong D band in the Raman spectrum with the intensity ratio of I_D/I_G >1 due to the moderately disordered crystal structure of graphene sheets. It is noted here that the intensity of the G band is significantly higher than that of the D band, *i.e.,* I_D/I_G <1, suggesting that the prepared graphene oxide has low defect content. Few defects could be formed due to stresses caused when the sample structure is distorted during exfoliation. Reduction in the D band means that a proper stress transfer has occurred, resulting in clean graphene oxide exfoliation from the activated sample. It can be inferred that the defects formed, electrochemically exfoliated graphene oxide is less when compared with chemically synthesized GO by Hummer's method

SEM analysis of exfoliated graphene

The scanning microscope SEM micrograph of the exfoliated graphene is shown in Figure 7. The micrograph shows a sponge-like structure with few layers not connected well with each other. This proves that the exfoliation of activated coke has occurred. The discontinuity in layers may occur due to the functionalization of the sample with an acid group, leading to the formation of graphene-like structure during exfoliation.

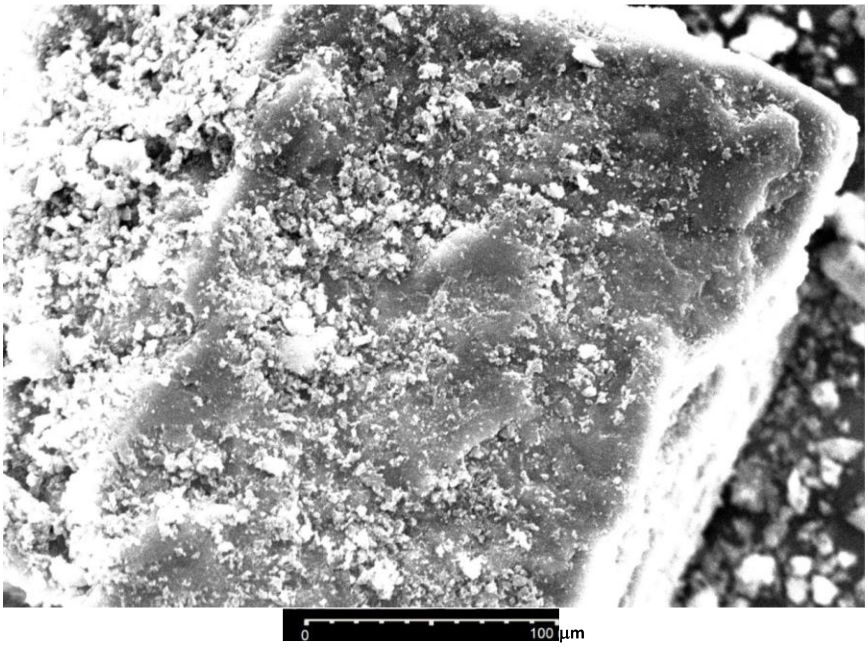

Figure 7. *SEM image of electrochemically exfoliated graphene oxide. Electrolyte concentration: 0.3 M H_2SO_4; applied voltage: 22 V; electrochemical exfoliation time: 8 h*

Energy storage application

The electrochemical energy storage capacitance was measured using an electrochemical workstation and a three-electrode system. The platinum wire and saturated calomel electrode (SCE) served as counter and reference electrodes, respectively. Specific capacitance was calculated by integrating the full CV voltammogram to determine the average value according to the equation (3):

$$C_\mathrm{p} = \frac{A}{2mk\left(V_2 - V_1\right)} \tag{3}$$

where C_p is specific capacitance in F g^{-1}, A is the area inside CV curve, m is the mass of the active material in g, k is the scan rate of CV in V s^{-1}, and V_2-V_1 is the potential window of the CV (total potential range).

Cyclic voltammograms for different electrolyte solutions are shown in Figure 8. Pet graphene oxide/Na_2SO_4, pet graphene/KOH and pet graphene oxide/H_2SO_4 systems showed regular rectangular shapes of curves observed for the various scan rates, which confirms nearly ideal capacitive behavior and excellent electrochemical reversibility. The area below the cyclic voltammetry curves increased with increasing scanning rate.

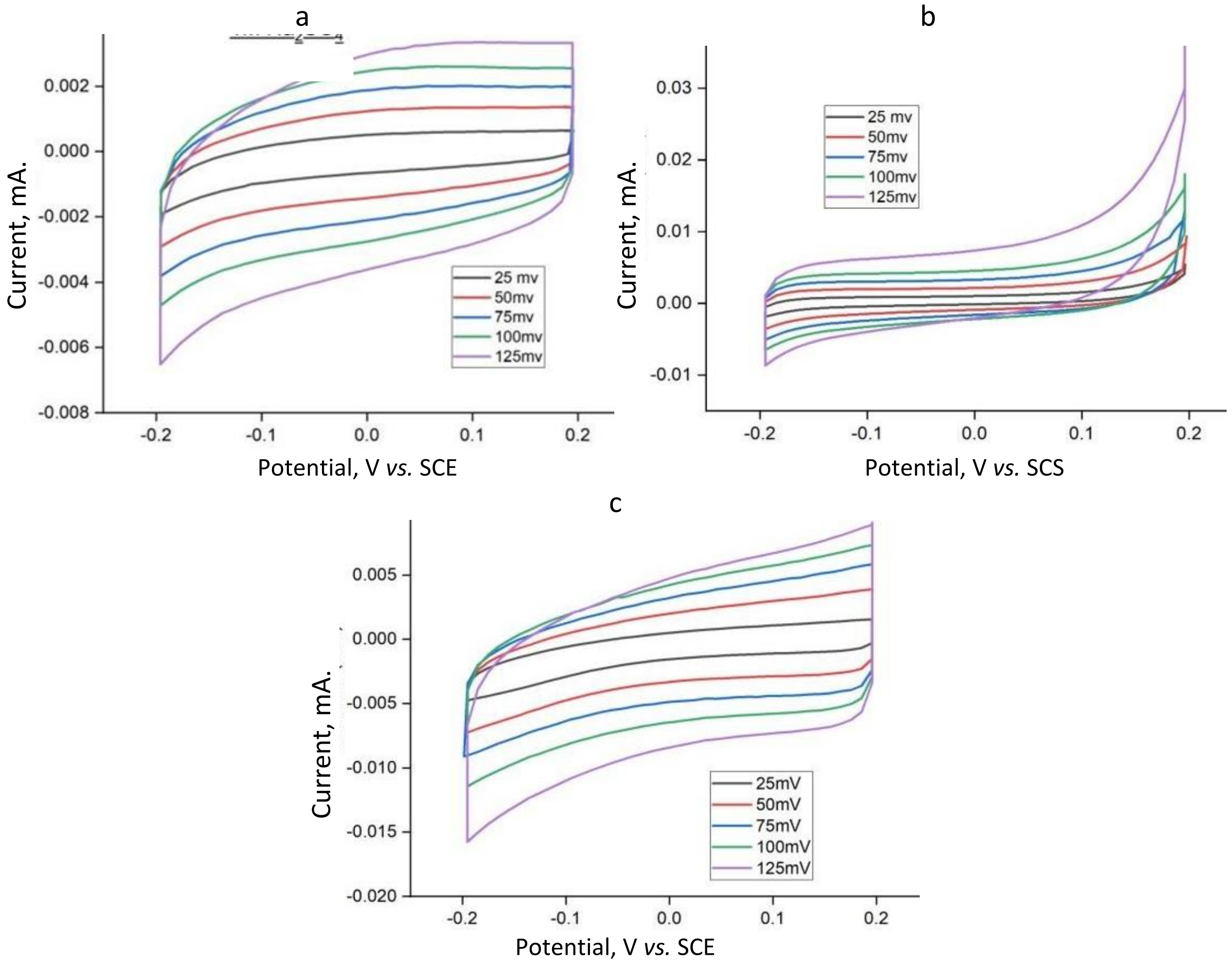

Figure 8. *Cyclic voltammograms at different scan rates of exfoliated graphene material in: (a) 1 M Na_2SO_4; (b) 2 M KOH; (c) 1 M H_2SO_4*

The specific capacitance values for three different electrolytes are shown in Figure 9.

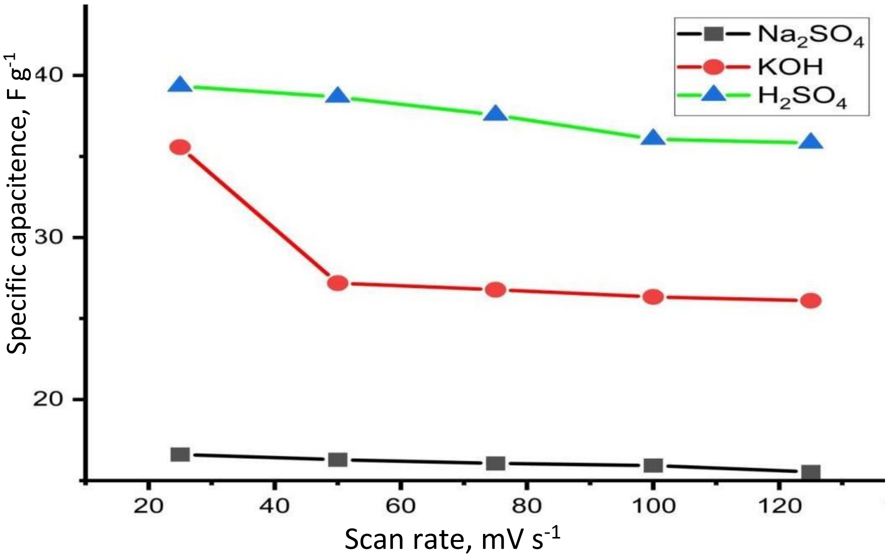

Figure 9. *Specific capacitance of synthesized graphene material at different scan rates and different electrolytes*

It can be noticed that the specific capacitance decreases with the increase in scan rate. As the scan rate increases, the diffusion of electrolyte ions into electrode internal structure and pores becomes difficult (diffusion limitation) and ineffective interaction between the electrolyte and electrode materials occurs; therefore, the specific capacitance value tends to decrease with an increase in the scan rate. This is due to polarization and depolarization of the electrode, which reduces the complete utilization of the surface area of the electrode when increasing the scanning rate. The maximum specific capacitance was 40 F g^{-1} at 25 mV s^{-1} scanning rate for the pet graphene used in the H_2SO_4 electrolyte system.

Conclusions

In this investigation, petroleum coke was activated using phosphoric acid and the activated pet coke was subjected to electrochemical exfoliation in an H_2SO_4 solution to produce a graphene-like structure material. Operating parameters for the activation of coke (pet coke to H_3PO_4 ratio, temperature and time of activation) and electrochemical exfoliation (voltage, concentration of H_2SO_4 electrolyte and time of exfoliation) were studied, defining the best-activated pet coke sample and the highest yield of exfoliated graphene. The exfoliated graphene material was tested for supercapacitor application in Na_2SO_4, KOH and H_2SO_4 electrolyte solutions, showing the highest specific capacitance of 40 F g^{-1} at 25 mV s^{-1} for the graphene/1 M H_2SO_4 system. It is concluded that graphene-like structure material derived from the exfoliation of activated pet coke can be used as supercapacitor material for electrochemical energy storage applications.

Consent for publication: *All authors have read and approved the manuscript to publish the work*

Availability of data and material: *All the data in the findings of this study are included within the manuscript.*

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Authors contributions

S. Dhana Priya:	carry out experiments, analysis and validation, rough drafting of manuscript
R. Saravanthamizhan:	conceptualization, investigation, methodology, manuscript revision
V. Manimozhi:	methodology and manuscript revision
T. Santhoshini Priya:	data interpretation and manuscript revision
N. Balasubramanian:	conceptualization and review of manuscript

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