The effect of cationic CTAB surfactants on the performance of graphene electrode for supercapacitor

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Abstract. Graphene is a two-dimensional sp2 bonded carbon nanostructure packed in a honeycomb crystal lattice. Graphene has a high theoretical surface area and electrical conductivity that is suitable for the electrode of supercapacitors. There are many methods to produce graphene, such as mechanical exfoliation using scotch tape, reduction of graphene oxide, and chemical vapor deposition. An alternative and simple method to produce graphene is through pyrolysis process. The previous study shows that the production of graphene from biomass via two-stage pyrolysis process results in an increase of the surface area; however, its capacitance is still low to be applied as the electrode for supercapacitor. This study aims to modification of graphene surface using cetyltrimethylammonium bromide (CTAB) as the surfactant. The graphene was produced from palm kernel shell via two-stage pyrolysis method (the first stage was at 350°C followed by the second stage at 900°C) using FeCl₃ as catalyst and ZnCl₂ as activating agent, resulting in 16% yield. Graphene was analyzed using Scanning Electron Microscope (SEM), Transmission Electron Microscope (TEM), Raman scattering, X-ray Diffraction (XRD), and Fourier Transform Infrared (FTIR). These analyses show that the two-stage pyrolysis produces multi-layered graphene. The surface properties were analyzed by nitrogen adsorption-desorption measurements, which show some mesoporous graphene product with a surface area of 351.27 m²/g. The result exhibited more hydrophilic graphene than the unmodified one, but according to the Cyclic Voltammetry (CV) analysis, the specific capacitance of modified graphene (11.91 Fg⁻¹) is lower than unmodified graphene (43.87 Fg⁻¹).

1. Introduction

Supercapacitors have become the most significant energy conversion and storage system in recent renewable and sustainable nanotechnology. Due to its large energy capacity, energy delivery in relatively short time, and longer lifetime, supercapacitors breakthrough in advance energy applications [1]. The energy storage in supercapacitors is based on ion adsorption (electrical double-layer capacitors, EDLCs) or fast and reversible Faradaic reactions (pseudocapacitors) [2]. EDLC store energy through the reversible adsorption of electrolyte ions on the surface of electrode materials by physical processes. Various carbonaceous materials, such as activated carbon and graphene, are used in EDLC [3, 4]. Activated carbon was extensively used as the electrode material in the construction of supercapacitors due to its large surface area and low cost. However, in such structures, there are a lot of carbon atoms that cannot be accessed by the electrolyte ions; consequently, this is a major factor that limits the specific
capacitance of activated carbon electrodes. Additionally, it is reported that the low electrical conductivity of activated carbon limits its applications in high power density supercapacitors and results in a low specific capacitance per area unit of material [5].

Therefore, an outstanding candidate for electrode material is graphene. Graphene is a two-dimensional \( sp^2 \) bonded carbon nanostructure packed in a honeycomb crystal lattice. Graphene has recently been investigated to exhibit exceptionally high thermal conductivity, electrical conductivity, and strength. Another outstanding characteristic of graphene is its exceptionally high specific surface area up to 2675 m\(^2\)/g [6,7]. Unfortunately, since the entire carbon structure is graphene, it is classified as a hydrophobic material [8]. Graphene surface modification that has been performed was modification graphene using splitting induced by UV irradiation [9], dispersed graphene oxide in polysulfone [10], sonicated graphene in water and acetone [11]. Previously, surfactants were used to surface modification of graphene. Furthermore, it has been previously reported that the surfactant can improve the interface property between electrode and electrolyte solution. Surface modification using surfactant was a simple method and can increase the wettability of graphene. In this work, we aim to alter the property of the graphene surface to be hydrophilic by a simple method using a common surfactant to improve the interfacial properties.

Surfactants are organic compounds consisting of two parts: a water-loving (hydrophilic) and a water-hating (hydrophobic) portions. Nowadays, such substances are used for these purposes: improving the wetting ability, emulsifying, increasing the inhibiting properties of the electrodeposition process, etc. Sodium dodecylbenzene sulfonate (SDBS), tetradecyl dimethyl betaine (BS14), and cetylpyridinium chloride (CPC) were used to functionalize graphene, but only tetradecyl dimethyl betaine functionalized graphene achieves a good dispersion in water. Tetradecyl dimethyl betaine is difficult to obtain. Furthermore, it has been previously reported that CTAB surfactant can improve the interface property between electrode and electrolyte solution [12]. Here, cetyltrimethylammonium bromide (CTAB), a positively charged surfactant with quaternary ammonium group, is used for the surface modification of graphene. In this study, we took sonication and dip-coating to study on the effect of mixing method of graphene and CTAB. In our best knowledge, this is the first paper that explains the surface of hydrophilic graphene is not the major requirement that can increase the specific capacitance of graphene. Specific capacitance is affected by the crystallinity and surface area of graphene.

2. Methods

2.1. Graphene synthesis

Palm kernel shell (PKS) was collected from PT Perkebunan Nusantara VIII Bogor, Indonesia. Ferric trichloride (FeCl\(_3\), 98%), hydrochloric acid (HCl, 37%), ethanol (Merck, 99.5%), and potassium hydroxide (KOH) (Merck, \( \geq \)84%) was used. Zinc chloride (ZnCl\(_2\), 99.8%) were bought from PT. Smartlab, Indonesia. Cetyltrimethylammonium bromide (CTAB, 99%) was obtained from Himedia Laboratories Pvt Ltd, Indonesia. Dried palm kernel shell was crushed using a ball mill to obtain coarse granules of 170-200 mesh. The raw material was mixed with urea as a nitrogen source with ratio of 1:1, 1 M FeCl\(_3\) as the catalyst, and ZnCl\(_2\) as activating agent with ratio of 2:1, all respect to the raw material (w: w). The mixture was stirred and heated on a hot plate (80°C) for 2 hours. Furthermore, the mixed material was dried in the oven for 2 hours. The mixed material then was put into a tubular furnace for carbonization and activation. The tubular furnace was set under nitrogen (99.998%) atmosphere, heated to 350°C and keep at this temperature for 60 minutes. This was the first stage of pyrolysis. Afterward, the temperature was increased to graphitization stage at 900°C and kept the temperature for another 90 minutes under flowing nitrogen. This is the second stage of the pyrolysis. Furthermore, HCl 2 M was added to the solution and stirred for 30 minutes. Consecutively, the solution was washed with demineralized water several times until the rinsed water reached pH of 7. The product was then dried at 105°C in a conventional oven for 24 hours to obtain graphene, denoted as unmodified graphene (G-PKS).
2.2. Surface modification of graphene
Cetyltrimethylammonium bromide (CTAB) was used in our study to modify the surface of graphene. According to reference [13], 500 mg of graphene was diluted to 1 mg/ml by water. The equivalent weight of CTAB was added to the solution, and then the suspension was sonicated for 1 h to form a uniform dispersion. Afterward, the suspension was separated by filtration through a Whatman Filter Paper No. 41 and the powder was dried in oven at 80°C for 24 h, denoted as modified graphene (G-PKS-S). Surface modification of graphene is also performed by dip-coating. Surfactant coatings are prepared by dipping graphene into a CTAB solution. The samples are then pulled out of the solution at a constant speed and were dried in a conventional oven at 80 °C for 10 minutes, denotes as modified graphene (G-PKS-DC).

2.3. Characterization of graphene
Scanning Electron Microscopy (SEM) was performed by using a HITACHI SU3500 instrument operating at 10 kV. Transmission Electron Microscopy (TEM) was performed by using a HITACHI H9500 to study the graphene morphology. Raman spectroscopy analysis was recorded on a Renishaw Raman Microscope. X-ray diffraction (XRD) patterns were obtained using a Bruker D8 advanced diffractometer with monochromatized Cu K radiation. The specific surface area was recorded according to adsorption-desorption isotherms performed by the Surface Area and Porosity Analyzer (NOVA 3200e, Quantachrome Instrument). The specific surface area was calculated according to the Brunauer-Emmet-Teller (BET) equation. Contact angle measurement used for hydrophobic/hydrophilic property or wettability characterization of the graphene surface. Fourier transform infrared spectroscopy (FTIR) was employed to explore the functionalization of graphene.

2.4. Electrochemical analysis
The electrochemical measurements were firstly conducted in a 6 M KOH aqueous solution in a two-electrodes system. The negative and positive electrodes were prepared by mixing the produced graphene with polyvinylidene fluoride (PVDF) at a weight ratio of 90:10. The above materials were coated onto a 1 cm² stainless steel mesh current collector and dried at 80°C for 8 h. Filter paper was sandwiched between two electrodes. The test was performed using KOH 6 M aqueous electrolyte solution under ambient conditions using a potentiostat (Gamry V3000). Electrochemical characteristic of samples was studied using Cyclic Voltammetry (CV), Galvanostatic Charge and Discharge (GCD), and Electrochemical Impedance Spectroscopy (EIS) techniques.

3. Results and Discussions
The morphology of graphene resulted by pyrolysis process was analyzed using electron microscopy (SEM and TEM). Figures 1 a, b, c show the SEM results of unmodified graphene (G-PKS), modified graphene by sonication (G-PKS-S), and modified graphene by dip-coating (G-PKS-DC), respectively. The G-PKS presents a continuous sheet-like structure of graphene layers that are stacked and folded together, which is beneficial for rapid ion and electron transport during the charge-discharge process of supercapacitors. After modification, the graphene layer is more piled, due to the interaction between nitrogen-doped graphene and CTAB. The interaction was revealed by FTIR analysis.

Morphological analysis of graphene from pyrolysis was also analyzed using TEM and HR-TEM. The TEM image of modified graphene in Figure 1c and d confirm that it consists of several layers with a distance of 0.354 nm between them. This is corresponding to the (002) interatomic distance of the graphitic carbon lattice [14]. The above results indicate that few-layer graphene has been successfully fabricated by two-stages pyrolysis method. The Selected Area Electron Diffraction (SAED) pattern in Figure 1f displays the representative hexagonal crystalline structure of graphene sheets, suggesting its high degree of graphitization.

The graphitic characteristic of G-PKS is confirmed by Raman spectroscopy. Three featured peaks located at 1362 cm⁻¹ (D-band), 1569 cm⁻¹ (G-band) and 2743 cm⁻¹ (2D-band) were obtained from the G-PKS sample (Figure 2a). The D-band is corresponding to the breathing mode of aromatic rings with
dangling bonds in planar terminations of disordered graphite and is related to the defects and disorders of structures in carbon materials, while the G-band is associated with the vibration of sp2-bonded carbon atoms in a two-dimensional hexagonal lattice [15]. The ratio between the G-band and D-band intensities ($I_G/I_D$) is proportional to the degree of crystallinity of carbon materials. The $I_G/I_D$ value is 3.1, suggesting the quite high graphitization degree of G-PKS, which is in accordance with the above SAED results.

**Figure 1.** SEM images of graphene (a) G-PKS, (b) G-PKS-S, (c) G-PKS-DC. TEM of graphene (d) G-PKS, (e) G-PKS-S, (f) SAED image of G-PKS.

Figure 2b shows the X-ray Diffraction (XRD) pattern of G-PKS and G-PKS-S. The XRD patterns of both graphene types show a peak at $2\theta \sim 26.5^\circ$, which indicates the atomic diffraction of (002) of graphitic structure. G-PKS and G-PKS-S showed the same intensity at $2\theta \sim 26.5^\circ$, suggesting that surface modification of graphene did not affect the crystallinity of graphene. XRD pattern of graphene shows impurities (such as cementite) peaks at $2\theta$ angle of 33.80$^\circ$ and 36.58$^\circ$. The impurity is produced by the decomposition of the FeCl₃ catalyst during the pyrolysis process.
Figure 2. (a) Raman spectrum of G-PKS, (b) XRD patterns of graphene

The hydrophilicity of graphene was measured using the contact angle (CA). As shown in Figure 3a, the CA of the modified graphene is obviously much smaller than that of the unmodified graphene. Water penetration time also demonstrates the wettability of the modified membranes, as shown in Figure 3a. The CA of unmodified graphene decreased slowly and reached 0° within 13 s. However, the CA of modified graphene by sonication and dip-coating decreases rapidly and reached 0° within 3 s and 6 s, which exhibit much higher hydrophilicity than the unmodified graphene. This phenomenon was resulted by the CTAB which is able to reduce surface tension between interfacial phases. In other words, CTAB has the ability to increase the miscibility between polar and non-polar phases. Thus, the adjustment of the modified graphene surface with micelle of CTAB takes advantage of improving the compatibility of graphene and water [16,17].

Figure 3. (a) Water contact angle and images of a water droplet on G-PKS, G-PKS-S, and G-PKS-DC (b) G-PKS, G-PKS-S, and G-PKS-DC FTIR spectra.
FTIR spectrum of produced graphene confirms the success of graphene surface modification. FTIR spectra of unmodified and modified graphene were shown in Figure 3b. In all curves, there is a broad peak at 3400 cm$^{-1}$, which is attributed to the N-H stretching vibration of the amine group. The peak at ~1600 cm$^{-1}$ is attributed to the N-H bending vibration of the amine group, and the peak at ~1200 cm$^{-1}$ is attributed to C-N stretching vibration. After the modification process, the transmittance of N-H and C-N bonds were decreased; it showed an increase in N-H and C-N bonds in graphene [18]. These strong evidences demonstrated that the CTAB was attached onto the surface of graphene. The increase in the intensity of the C-N bond is quite significant, the C-N bond of nitrogen-doped graphene is coupled with the C-N bond of the amine bond on CTAB and the C atom bond on CTAB with N on nitrogen-doped graphene. This bonding reduces the distance between the graphene layers and reduces the active surface area of graphene. The peak at 1600 cm$^{-1}$ is attributed to the C = C stretching vibration. The intensity of the C = C bond also increases; this shows the existence of a bond between C in the hydrophobic group (C$_{16}$H$_{33}$) in CTAB with the C atom in graphene [19]. FTIR peak G-PKS-S is significantly increased while G-PKS-DC is almost similar compared with G-PKS due to sonication cause the CTAB was attached onto the surface of graphene more strongly than dip coating.

The specific surface area of graphene was measured using nitrogen adsorption-desorption isotherms. If this graphene will be used as electrodes of the supercapacitor, it needs a large surface area beside a high degree of crystallinity [20]. Based on the calculation using the BET method, the surface area of G-PKS is 351.26 m$^2$/g, G-PKS-S is 187.82 m$^2$/g, G-PKS-DC is 302.52 m$^2$/g. The surface area of graphene has decreased after CTAB addition, due to the interaction between CTAB and graphene. It stacked the graphene layers and reduced the active surface area of graphene. The surface area of modified graphene by sonication has also decreased since sonication during 30 or 60 minutes breaks the graphene large sheets into rather small pieces. These results are in accordance with the above FTIR results.

![Figure 4](image_url)

*Figure 4.* (a) CV curves of unmodified graphene at various scan rates ranging from 2 to 10 mV/s, (b) CV curves of unmodified and modified graphene at scan rate 2 mV/s, (c) Charge discharge curve and (d) Nyquist plot of unmodified and modified graphene.
The electrochemical characteristics of the EDLCs made of unmodified and modified graphene were examined using CV, GCD, and EIS. Cyclic Voltammetry was used to observe the cell characteristics and its capacitance. The measurements were performed at room temperature within the potential range of -0.2 to 0.8 V and over a scan rate of 2 to 10 mV/s. Figure 4a shows the voltammograms of the unmodified graphene symmetrical cell at five different scan rates (2, 4, 6, 8, and 10 mV/s). Figure 4a demonstrates that the current response increased with the scan rate. Table 1 shows the $C_{sp}$ values determined using Eq. (1) and the voltammograms of unmodified graphene symmetrical cell obtained at different scan rates. All cells show a common trend of decreasing $C_{sp}$ with increasing scan rate. It is well known that for very low scan rates, the $C_{sp}$ values are high because the ions have a much longer time to penetrate and reside in all the available electrode pores and form electrical double layers, which are needed to generate higher capacitance [21].

Figure 4b presents the CV curves of unmodified and modified graphene, and Figure 4c presents their GCD curves. The shape of the voltammograms for all the cells is quasi rectangular, representing a typical voltammogram of the Electrical Double-Layer Capacitor [22]. Comparing to the voltammograms of modified graphene by sonication (G-PKS-S), and modified graphene by dip-coating (G-PKS-DC) cells in Figure 4b, it can be observed that the G-PKS cell has a broader voltammogram area. These results indicate that the G-PKS cell has better cycle reversibility and higher electrical double-layer capacitance stability during the charge and discharge processes compared to the other cells. The specific capacitance of the produced graphene was calculated from cyclic voltammogram according to Eq. (1) [23]:

$$C = \sum |I| \cdot \Delta t / m \Delta V$$  \hspace{1cm} (1)

The specific capacitance of unmodified graphene, modified graphene with sonication and modified graphene with dip-coating respectively are 43.87, 11.91, and 37.76 F/g. After surface modification, the specific capacitance of graphene decreases. Since the presence of CTAB decreases graphene surface area, therefore it reduces the site of the electrochemical reaction, thus, reduces the occurrence of the electrochemical reaction. The reduction in electrochemical reactions is proportional to the reduction in electric current, so the amount of electric charge stored is also reduced.

**Table 1.** Specific capacitance of unmodified graphene at various scan rates

| Electrode         | 2 mV/s | 4 mV/s | 6 mV/s | 8 mV/s | 10 mV/s |
|-------------------|--------|--------|--------|--------|---------|
| Unmodified graphene | 43.87  | 20.12  | 14.84  | 13.88  | 10.33   |

The GCD curves of all the graphene cells recorded at a current density of 1 mA cm$^{-2}$ are shown in Figure 4c. As seen in this figure, all cells show a similar symmetrical triangular curve with a nearly linear variation of voltage as a function of time during charge and discharge. This type of curve is typical for carbon-based supercapacitors. However, despite having a similar shape, the curves of the G-PKS cells show higher peak potential than G-PKS-S and G-PKS-DC cells, as shown in Figure 4c. These observations indicate that the unmodified graphene cell has a higher capacitance than modified graphene. These results are in good agreement with the obtained CV results.
Table 2. Impedance parameters of graphene cell

| Parameter | Unit          | Value                  | Value                  | Value                  |
|-----------|--------------|------------------------|------------------------|------------------------|
|           |              | Unmodified graphene    | Modified graphene by   | Modified graphene by   |
|           |              |                        | sonication             | dip-coating            |
| R1        | Ohm          | 3.534                  | 1.022                  | 0.845                  |
| R2        | Ohm          | 18.61                  | 200                    | 48.97                  |
| CPE1      | S*s^a        | 5 x 10^{-4}            | 6 x 10^{-5}            | 3.95 x 10^{-1}         |
| a1        |              | 7.53 x 10^{-1}         | 8.83 x 10^{-1}         | 9.15 x 10^{-1}         |
| CPE2      | S*s^a        | 1.11 x 10^{-1}         | 7.02 x 10^{-1}         | 6 x 10^{-5}            |
| a2        |              | 8.52 x 10^{-1}         | 9.29 x 10^{-1}         | 8.78 x 10^{-1}         |
| R3        | Ohm          | 35.41                  | 41.53                  | 26.95                  |

The EIS of graphene-based supercapacitor cells has been conducted in frequency range of 100 kHz to 100 mHz. Figure 4d shows the Nyquist plots of graphene-based supercapacitor. In the low-frequency region, the Nyquist plot is a straight line for an EDLC supercapacitor. The more vertical the line, the more closely the supercapacitor behaves like an ideal capacitor. Compared to the G-PKS and G-PKS-DC cells, the G-PKS-S cell results in the straightest line with an almost 90° angle, which is the characteristic of better capacitive behavior. However, G-PKS-S has largest semicircular portion that indicates G-PKS-S has high charge-transfer resistance, leading to poor electron transfer through the surface. Adding CTAB impeded the electron transfer due to CTAB has no property of direct improvement of the electrical conductivity. The semicircle diameter of the impedance loop represents the charge transfer resistance in the electrode material. In the high-frequency region, the curve intercept on the real axis is the Equivalent Series Resistance (ESR) [24]. The fitting equivalent circuit model by the coupled nonlinear Schrödinger equation (CNLS) method is displayed in the inset of Figure 4d. The whole capacitor circuit is constituted by R1, R2, CPE1, CPE2, and R3. The R1 is the sum of the contact resistance and material resistance (electrode materials, electrolyte, and separator). The R2 represents the charge transfer resistance at the electrode-electrolyte interface [25]. The R3 is the mass transfer resistance at electrolyte-electrode interface. The charge and mass transfer resistances (R2 and R3) increase after surface modification. It indicates that the CTAB attached on graphene surface hinders mass transfer to the graphene surface. The EIS results further demonstrate that the synergy effect between the large surface area and good electrical conductivity of electrode materials enhances the rate of electron and ion transport.

4. Conclusion
Nitrogen-doped graphene has been synthesized successfully through an easy, low cost and reliable two-stages pyrolysis from palm kernel shell. The graphene morphology shows a 2D structure. Raman studies provide evidence of the presence of graphene. XRD confirmed the formation of graphene. The addition of CTAB surfactant in the surface modification of graphene process enhances the hydrophilicity of graphene because CTAB has the ability to improve the miscibility between polar and non-polar phases. However, the specific surface area of graphene from PKS decreases from 351.26 m²/g to 187.82 m²/g. It causes the specific capacitance of graphene to decrease from 43.87 F/g to 11.91 F/g.

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