Simultaneous Electrochemical Exfoliation and Chemical Functionalization of Graphene for Supercapacitor Electrodes

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Abstract

The demand for efficient electrochemical energy storage technology, such as supercapacitors, continues to increase as both the energy and power demands of devices grow. Graphene has attracted wide interest in addressing this energy challenge due to its high conductivity and specific surface area. However, in reality the hydrophobic properties and the restacking of the graphene sheets during device manufacture leads to significantly lower storage performance than that theoretically predicted for isolated sheets. Herein, functionalized graphene was prepared by a convenient one-pot process, where graphene was functionalized with aryl diazonium salts (4-nitrobenzenediazonium tetrafluoroborate (NBD) and 4-bromobenzenediazonium tetrafluoroborate (BBD)) simultaneously during oxidative electrochemical exfoliation of graphite. It was found that the specific capacitance for functionalized graphene was significantly improved compared to pristine graphene due to the introduction of pseudocapacitance by the aryl diazonium salts. The dispersibility of functionalized graphene in water was also found to be improved, implying a better hydrophilicity. NBD functionalized graphene which had been exfoliated/functionalized for a total of 30 minutes exhibited the best energy storage properties with a 5 times increase in specific capacitance (17 mF cm^{-2}) compared to pristine graphene (3 mF cm^{-2}).

Introduction

The development of green, renewable energy conversion materials and especially materials for energy storage which can balance energy supply and demand is of paramount importance due to increasing demand [1]. Being developed for complimentary usage alongside batteries, supercapacitors boast features such as high power density, long cycle life, safety, and temperature tolerance [2]–[4]. However compared to batteries, supercapacitors are low in energy density. In order to increase the energy density, the specific capacitances need to be increased, which is generally dependent on the active materials of the electrodes (e.g. their surface area, electric conductivity, pore sizes and etc.). Apart from exploring new materials, another way to improve the energy density is to chemically modify existing electrode materials.

Graphene, a two dimensional (2D) monolayer of carbon atoms which are packed into a honeycomb lattice was first isolated from graphite by Geim & Novoselov using scotch tape exfoliation [5], from which they overturned the theory of Landau and Peierls that 2D crystals were thermodynamically unstable and could not exist [6][7]. The remarkable physiochemical properties (e.g. high electrical, thermal conductivity and high specific surface area) of graphene have attracted great interest and has made it promising in energy storage applications, such as supercapacitors [8][9].

Although graphene is an ideal material for supercapacitors due to its high specific surface area, most of the surface area is not accessible to ions due to the restacking of graphene and thus leading to low specific capacitance [10]. Recently many reports have been published on graphene composites and functionalized graphene to improve this ion-accessibility. Herein it is speculated that by functionalization of graphene with aryl diazonium salts, the restacking can be reduced (for example, the inter layer spacing between the graphene layers is increased by the grafted phenyl

group of the diazonium salts) and the properties of graphene electrodes (such as energy density) can be improved.

Aryl diazonium salts reported by Pinson and co-workers in 1992 are ideal chemicals for surface modification of electrodes [11]. The chemistry of aryl diazonium salts has since been widely reported due to the ease of preparation, rapid reaction, and strong aryl-substrate covalent bonding [12], [13]. Another advantage of the grafting of aryl diazonium is that they are able to contain a wide variety of functional groups and thus able to improve the surface chemistry of the electrodes. For example the functional group of aryl diazonium salts can be substituted by a hydrophilic –SO₃H group which increases the electrolyte wettability of electrodes [13]. In addition, the functional groups can also introduce pseudocapacitance to the electrode and therefore improve the specific energy density.

The reactions of aryl diazonium onto surfaces undergo two mechanisms: the cleavage of the diazonium carbon bonds ($^+\text{N}_2\text{-C}$) which requires an electron donation from the surface to form aryl radicals, and the attack of the free radicals on the surface. The formation of the free radical can be initiated electrochemically, chemically, and spontaneously, but for the spontaneous reaction to happen the surfaces need to be conductive. As the reaction proceeds the radicals can bind with the aryl groups already immobilized on the surface, forming multilayers [14]. They can also react with themselves forming polymers which can be physically adsorbed onto the surface.

The functionalization of graphene with aryl diazonium has been previously reported [15], [16]. However, no research has so far reported the effects of functionalization time of aryl diazonium salts on the electrochemical properties of graphene supercapacitors where graphene is exfoliated and functionalized simultaneously. In this article, the graphene will be electrochemically exfoliated and functionalized at the same time similar to that previously demonstrated [15]. The

electrochemical properties of functionalized graphene supercapacitors are investigated for differing functionalization times with aryl diazonium salts. Herein, we used two commercially available diazonium salts NBD (4-nitrobenzenediazonium tetrafluoroborate) and BBD (4-bromobenzenediazonium tetrafluoroborate) to functionalize graphene under different reaction time (10, 30, 60 minutes). Both NBD and BBD are easier to characterize thanks to their characteristic functional groups $-\text{NO}_2$ and $-\text{Br}$, while anthraquinone was used in previous examples [15], which, like electrochemically exfoliated graphene, has only benzene rings and oxygen [12].

1 Experimental

1.1 Preparation of functionalized graphene

10 mM of BBD or NBD was dissolved in 100 mL of water, with 0.1 M of H_2SO_4 and 300 μL of 1 M Na_2SO_4 added to assist the exfoliation. Electrochemical exfoliation and simultaneous functionalization was then carried out in this solution using a Pt wire cathode and graphite foil (L x W: 5 x 1.5 cm) anode. The distance between the two electrodes was kept at 2 cm throughout the exfoliation process and a voltage of 10 V was applied to the system. After the graphite was exfoliated and functionalized for 10, 30 and 60 minutes (which were subsequently named N10, N30, N60 for NBD functionalized graphene and B10, B30, B60 for BBD functionalized graphene), the exfoliated and functionalized graphene was separated from the solution and rinsed thoroughly using a PTFE membrane and a vacuum filter. The product was finally dried overnight at room temperature.

1.2 Assembly of supercapacitors

The functionalized graphene was dispersed in 1:1 isopropanol (IPA) and H₂O and sonicated (37 kHz, 40% power) for 2 h. The dispersion was then centrifuged at 4000 rpm for 30 minutes and a known volume of the supernatant was filtered through a PVDF membrane filter using a syringe pump at a rate of 5 mL h⁻¹. The membrane was then dried in a vacuum oven overnight. The average weight of functionalized graphene on each membrane was 0.3 mg. Coin cell assembly was prepared by stacking two symmetrical membranes back-to-back with the active materials contacting the current collector in standard CR2032 coin cell hardware using the same method described previously [17]–[19]. 6 M KOH was added to the electrode before sealing the coin cells using a Digital Pressure Controlled Electric Crimper (MSK-160D).

1.3 Electrochemical analysis

Cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and Galvanostatic charge/discharge (GCD) were performed using an Ivium CompactStat. The specific capacitances were determined using GCD results at a current density ranging from 0.3 mA cm⁻² to 10 mA cm⁻². CV was carried out at a scan rate of 5, 10 and 100 mV s⁻¹. For both GCD and CV tests, a potential window from 0 to 0.8 V was used. EIS was performed at a frequency range of 0.01 Hz to 100 kHz with amplitude of 5 mV.

1.4 Characterization

The surface morphology of the pristine and functionalized electrochemical exfoliated graphene (EEG) was characterized using a MIRA3 TESCAN scanning electron microscope (SEM) and a JPK NanoWizard atomic force microscope (AFM) with QI mode being used. For AFM, the supernatant described above was first spin-coated onto a silicon wafer at a speed of 1500 rpm for 60 s. EEG and the functionalized graphene were also characterized with X-ray photoelectron

spectroscopy (which was equipped with a monenergetic Al-K α X-ray source at a pass energy of 20 eV). The XRD patterns were obtained the PANalytical X'Pert Pro diffractometer with Cu-K α radiation source operating at 40 kV and 40 mA whilst spinning in the range $2\theta = 3.01^\circ$ to 101.98° , with a step size of 0.033° and a scan step size of 530 s/step.

Pristine and functionalized EEG was drop cast onto Si/SiO₂ (300 nm thickness of oxide) wafers followed by drying in a vacuum oven. Confocal Raman spectroscopy was carried out using a Renishaw inVia microscope with a 532 nm (2.33 eV) excitation at a power of 1 mW with a 100 $\times$ objective and a grating of 1200 l/mm.

2 Results and Discussion

2.1 Characterization

Figure 1 a)-c) show representative SEM images of powder samples of EEG, B60 and N30. Only N30 and B60 are shown here because they possess better electrochemical performance than other samples. It can be seen that B60 and N30 have more wrinkles, which according to the literature results from the strain generated by intense functionalization[16], [20], [21]. Figure 1 d)-f) show SEM images of indicated graphene membranes. Compared to EEG, B60 and N30 have smaller flake sizes, which agrees with the AFM images (see Figure 1 g)-i)). From the AFM images, B60 and N30 have smaller flake sizes ($\sim 2 \mu\text{m}$) compared to EEG ($\sim 4 \mu\text{m}$). It is suggested that the functionalized graphene disperses better in the solvent while EEG forms clumps and thus the sonication is more efficient for functionalized graphene (see Figure S1), which is supported by the trend of reducing flake sizes as the functionalization time increases (see Figure S2 for representative change of flake sizes as a function of functionalization time of NBD with graphene).

The analysis of Raman maps helps with the estimation of successful functionalization. Statistical analysis of Raman mapping data was carried out in order to estimate the changes in the surface chemistry of graphene after functionalization. Figure 2 a) and b) represent scatter plots of Raman peak parameters. Each indicated sample has a scatter plot of 156 points (10 x 10 μm). For both Figure 2 a) and b), the increased functionalization time has caused the broadening of G peak and the shifting of G peak to a higher frequency, which indicates increased disorder [22], [23]. This increased disorder is attributed to the formation of covalent bonds resulting from diazonium functionalization. The scattered points for both NBD and BBD functionalized graphene converge as the time of functionalization increases. This suggests that the surfaces of the graphene flakes are becoming saturated with functional groups and thus the surface chemistry of each flake is becoming more uniform. By comparing Figure 2 a) and b), it is also realized that NBD is more reactive than BBD since the data points for NBD functionalized graphene converge at a reaction time of 10 mins while the ones for BBD are still divergent. This is consistent with previous literatures which show that NBD has a higher reaction rate than BBD does [24]–[26].

The 2D peak position was also plotted against G peak position as shown in Figure 2 c) and d). For both NBD and BBD functionalized graphene, the 2D peak position shifts to lower frequency while G peak position shifts to a higher frequency. This indicates that both functional groups have offset the initial p-doping in EEG and made it become more n-type doped, resulting from the donating of electrons of either nitro or bromo groups in diazonium salts. The shifting of the 2D peak is attributed to the strains of functional groups, which is consistent with the increased wrinkles after functionalization as shown in Figure 1 a)-c) [16], [27].

Histograms of D and G peak intensity ratios for NBD and BBD functionalized graphene are shown in Figure 2 e) and f), respectively. For both NBD and BBD functionalized graphene, the intensity

ratio increases with increasing functionalization time, which suggests increased defects as expected. The increasing D peak intensity indicates the presence of defects which can result from physical damage or from the formation of covalent bonds [22], [28]–[32]. Here, the increased D and G peak intensity ratio is attributed to formation of covalent bonds rather than physical damage as the functionalization process does not cause physical damages [22].

To further investigate the successful grafting of aryl diazonium salts onto graphene and to determine the bond types, XPS analysis was conducted. XPS spectra of N30 and B60 are used as representative XPS spectra for NBD and BBD functionalized graphene. Figure 3 a) and b) show XPS spectra of N1s for N30 and Br3d for B60 respectively. Both spectra are fitted with Lorentzian-Gaussian peaks at 70:30 ratios. From N1s for N30, 3 peaks are noticeable. These 3 peaks at 400.1 eV, 401.9 eV and 405.8 eV are attributed to -N=N- bonds, -N-C=O bonds, and NO₂, where -N=N- groups come from the attack of NBD to those NBD grafted on graphene surfaces and NO₂ are the nitro groups of NBD[33], [34]. As demonstrated in Figure 3 b), the presence of aryl-Br groups at 70.3 eV indicates the grafting of aromatic ring to graphene and the peak at 71 eV suggests the occurrence of C-Br groups at the polymer chain ends. From the survey scan of N30 and B60 in Figure 3 c) and d), nitrogen is detected for N30 and both nitrogen and bromine for B60.

These functional groups are believed to cause the increase in the interlayer distances as is evident from the extra peaks appearing at $2\theta \sim 10^\circ$ for both N30 and B60 in the XRD patterns (Figure 3 e)) compared to EEG. It is suggested that these peaks correspond to the (001) plane which are similar to the characteristic (001) crystal plane of graphene oxide (GO). The relative intensity of (001) peak for N30 is greater than that for B60 due to the fact that the NBD is more reactive than BBD resulting in more surfaces being functionalized and thus there are more interlayer spacing

being increased. Additionally the contact angle data shown in Fig. 3f shows that after functionalization the N30 and B60 samples are found to be more hydrophilic compared to unfunctionalized EEG which confirms the change in surface energy after attachment of the functional groups as well as indicating that the functional groups for both N30 and B60 increase hydrophilicity and are expected to improve electrolyte wetting.

2.2 *Electrochemical properties*

To determine the effect of functionalization time on the specific capacitance of NBD and BBD functionalized graphene, and also to compare the specific capacitance of NBD and BBD functionalized graphene, specific capacitances are plotted against current densities for indicated samples as shown in Figure 4 a) and b). The specific capacitances are represented by mF cm^{-2} rather than F g^{-1} in order to reduce error since the mass of the materials on the PVDF membranes are low. Each data point is based on an average of 3 devices made from the same materials and the error bars are obtained from the standard deviations.

For NBD functionalized graphene, the specific capacitance increases with functionalization time for the first 30 minutes, and reaches its highest specific capacitance of 17 mF cm^{-2} at 30 minutes at a current density of 3 mA cm^{-2} . This indicates an improvement in specific capacitance by a factor of $\sim 5\text{-}6$ after the functionalization. However, it decreases dramatically as the functionalization time increases further to 1 h. This suggests the specific capacitance can be reduced if the graphene is too saturated with functional groups, because the excessive functionalization will decrease the conductivity of graphene [16]. For BBD functionalized graphene, specific capacitance also increases with reaction time, and B60 has the highest specific capacitance of 16 mF cm^{-2} at a current density of 0.3 mA cm^{-2} . Note that NBD functionalized graphene reaches its optimal specific capacitance for a reaction time shorter than BBD

functionalized graphene. This is because NBD is more reactive than BBD and thus forms an aryl film on graphene faster. This is consistent with the scatter plots of Raman mapping in Figure 2 a) and b), where scatter plots for NBD functionalized graphene converges earlier than those for BBD. Since N30 and B60 have higher specific capacitances compared to other samples, the following paragraphs will focus on comparing N30 and B60.

From Figure 4 c), it can be seen that B60 has a larger semicircle in the high frequency region compared to N30, meaning a larger charge transfer resistance [35]. In Figure 4 d), the impedance of B60 and N30 is very similar at low frequency. However, as the frequency increases to about 1 Hz, the impedance of B60 becomes greater than that of N30. This explains the phenomenon in Figure 4 a), where the specific capacitance of B60 decreases dramatically and is much smaller than that of N30 as the current density increases (frequency increases). It is also noticed in Figure 4 a) that the N30 has a lower slope compared to that of B60. This is because, as shown in the bode plots in Figure 4 d), the phase angle of N30 is closer to 90° compared to B60, indicating that N30 has more capacitance contribution from electric double layer capacitance. Both N30 and B60 are a combination of pseudocapacitance CPE2 and double layer capacitance CPE1. The equivalent series resistances R1 for N30 and B60 are similar, which are both about 0.3Ω , while charge transfer resistance R2 of B60 (89.87Ω) is much larger than the one of N30 (21.35).

The electrochemical properties of N30 and B60 are investigated using cyclic voltammetry and charge discharge techniques. From Figure 5 a) two plateaus at around 0.2 V and 0.6 V respectively are observed at a current density of 0.3 mA cm^{-2} for N30, which, according to Andinet and co-workers, is due to redox reaction of the nitro groups [16]. For B60 (Figure 5 b)), although no obvious plateaus are measured, the charge-discharge curve at 0.3 mA cm^{-2} deviates from a symmetric triangular shape, which is also an evidence of faradaic reaction. The IR drops of B60

are also greater than those of N30, indicating greater resistance, which agrees with the Bode plots and Nyquist plots shown previously. The CV curves for N30 and B60 (Figure 5 c) and d)) both also show typical faradaic pseudocapacitive behavior (distortion from triangular shapes). It can be seen from Figure 5 e)-g) that the functionalization does not affect the coulombic efficiency. Both N30 and B60 have excellent coulombic efficiency even after 10000 cycles. The capacitance retention for N30 and B60 increases after 8000 cycles and 4000 cycles respectively, which is ascribed to the intercalation of ions. As proved in Figure 3 f) that N30 is less hydrophilic than B60, and thus N30 has less ions intercalated resulting in less increase in capacitance when compared to B60.

Conclusions

In summary, electrochemical exfoliated graphene was functionalized with two aryl diazonium salts (NBD and BBD), which were then used as electrodes for supercapacitors. The effect of reaction time between diazonium salts and graphene to the specific capacitance of a supercapacitor was studied. It was found that the optimal reaction time for NBD and graphene was 30 mins and that for BBD and graphene was 60 mins. When at a current density of 3 mA cm^{-2} , N30 has a specific capacitance of 17 mF cm^{-2} and B60 16 mF cm^{-2} , both of which were about 6 times higher than the specific capacitance of EEG (3 mF cm^{-2}). For N30, the effect of increase in impedance due to the functionalization did not dominate the effect of pseudocapacitance, and thus the specific capacitance has reached the highest. BBD had slower reaction rate than NBD and thus it took longer time for it to reach its highest specific capacitance. B60 is less preferred than N30 since its capacitance decreases dramatically when at higher current density.

Supporting Information

Schematics of EEG, B10, B30, B60, N10, N30, N60 dispersed in 1:1 IPA and H₂O. Histogram of flake sizes of EEG and NBD functionalized graphene. Representative Raman spectra. XPS spectra of C1s of N30, B60, survey scan of N30 and survey scan of B60.

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Figures

Figure 1. Representative SEM images of powder samples a) EEG, b) B60 and c) N30; Representative SEM images of filtered d) EEG membrane, e) B60 membrane and f) N30 membrane; Representative AFM images (height images) of spin coated g) EEG, h) B60 and i) N30 on silicon wafers.

Figure 2. Raman mapping data for NBD functionalized graphene, BBD functionalized graphene as well as EEG (see Figure S3 for representative Raman spectra for each sample). FWHM of G peak versus G peak position of NBD functionalized graphene (a) and BBD functionalized graphene (b). 2D peak position versus G peak position for NBD functionalized graphene (c) and BBD functionalized graphene (d). Histogram of D to G peak intensity ratio for NBD functionalized graphene (e) and for BBD functionalized graphene (f). The data for EEG in (a-d) is the same.

Figure 3. High resolution XPS spectra of a) N1s of N30 and b) Br3d of B60; Survey scan of c) N30 and d) B60; XRD patterns for filtered membranes of indicated samples and f) contact angle measurements for water droplets on indicated samples.

Figure 4. a) and b) Specific capacitance versus current density for indicated samples; c) Nyquist plot of N30 and B60 and fitting of their Nyquist plots according to the model shown in e) ; d) Bode plots of B60 and N30 and e) the equivalent electric circuit for N30 and B60, where R_1 is the equivalent series resistance (ESR), R_2 the resistance of charge transfer resistance, R_3 the leakage resistance, $CPE1$ the double layer capacitance, $CPE2$ the pseudocapacitance and W_1 the Warburg element denoting the ion diffusion into porous electrode[36], [37].

Figure 5. Galvanostatic charge-discharge curves for a) N30 and b) B60 at different current densities from 0.3 to 1 mA cm⁻²; cyclic voltammetry curves of c) N30 and d) B60 at scan rates of 5, 50 and 100 mV cm⁻²; e)-g) coulombic efficiency and capacitance retention for EEG, N30 and B60.