

1-Pyrenebutyric Acid Functionalized Reduced Graphene Oxide (1-Pb-Rgo) Energy Storage

Ellie Yi Lih Teo, Mashitah Mohd Yusoff and Kwok Feng Chong

Abstract Supercapacitors are a class of energy storage device which has high energy density and high power density. As a material with unique 2D structure as well as outstanding physical properties such as high electrical conductivity and large surface area, graphene demonstrates great potential to be the electrode material for supercapacitors. Despite graphene showing theoretical surface area as high as 2630 m²/g, results acquired showed that not all the surface area were utilized. This could be due to the tendency of the graphene layers to restack. In this work, 1-pyrenebutyric acid (1-PB) was anchored to graphene with the pyrenyl group via π - π stacking to prevent the restacking of graphene layers. The successful functionalization of 1-PB on the hydrophobic surface of rGO was characterized with UV-Vis Spectroscopy and Fourier Transformed Infrared Spectroscopy (FTIR). The electrochemical performance of 1-PB-rGO was studied through cyclic voltammetry (CV), galvanostatic charge-discharge (CD) and electrochemical impedance spectroscopy (EIS). Using 6 M KOH as the electrolyte, we obtained an enhanced specific capacitance for 1-PB-rGO. These findings indicates that the non-covalent functionalization of 1-PB on rGO enhances the capacitive storage ability and it show potential as an electrode material in the energy storage application.

Keywords Reduced graphene oxide · Non-covalent functionalization · Energy storage

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Introduction

In the modern era of technology where portable electronics are a current trend together with the depletion of fossil fuel have led to the search for a dependable and durable energy storage solution. Among the various solutions which are being explored, supercapacitor have gained the attention of the research community. The supercapacitor is a class of energy storage device which has a high energy density as compared to conventional capacitors and a higher power density compared to batteries.

Since its discovery by Andre Geim and Konstantin Novoselov, graphene has become a sensational material due to its exceptional properties. Graphene is a single layer of sp^2 bonded carbon atoms arranged in honeycomb crystal lattice. It possess exceptional properties such as very high specific surface area ($\sim 2630 \text{ m}^2/\text{g}$) and high electrical conductivity which fits the criteria as the electrode material of the supercapacitor [1]. This results in graphene to be highly explored in the application of energy storage.

However graphene tends to agglomerate as a result of the Van der Waals interaction. In order to prevent this, functionalization of graphene is performed by the covalent or non-covalent modification technique in order to improve their solubility, self-assembly properties and in applications [2]. The non-covalent functionalization is preferred as it does not disrupt the conjugation of the graphene sheet and improves its stability [3]. A few works have been reported on the non-covalent functionalization of graphene with pyrene derivatives. Xu et al. [2] functionalized graphene with 1-pyrenebutyric acid through a simultaneous functionalization and reduction method. Supercritical carbon dioxide was used in the research of Li et al [4] to assist in the functionalization process. While there are a few literatures which reported on the different methods of functionalization, only Ghosh et al. (2012) and An et al. (2010) reported on the application of pyrene derivatives functionalized graphene as energy storage device. They studied on the effect of 1-pyrenecarboxylic acid functionalization of graphene on its capacitive storage ability and reported specific capacitance value of 200 and 120 F/g respectively [1, 5].

In this work, 1-pyrenebutyric acid, a pyrene derivative which is reported to interact with graphite with the pyrene group via π stacking is used to functionalize reduced graphene oxide (rGO). 1-PB was anchored to the hydrophobic surface of reduced graphene oxide (rGO) through a simple sonication process at room temperature. Reduced graphene oxide was successfully functionalized with 1-pyrenebutyric acid (1-PB) with this method. The application of 1-pyrenebutyric acid functionalized reduced graphene oxide (1-PB-rGO) is studied electrochemically with cyclic voltammetry (CV), galvanostatic charge-discharge (CD) and electrochemical impedance spectroscopy (EIS).

Experimental

Chemicals

All chemicals used in this experiment were purchased from Sigma-aldrich unless otherwise stated and used as received.

Graphene Oxide Preparation

Briefly, 4.0 g of graphite powder was added into a mixture of concentrated sulfuric acid, H_2SO_4 (30 mL), potassium persulfate, $\text{K}_2\text{S}_2\text{O}_8$ (6.0 g) and phosphorus pentoxide, P_2O_5 (6.0 g). The mixture was heated at 80 °C and kept stirred for 6 h using oil bath. After 6 h, the solution was cooled and diluted with 2 L of deionized water. The solution was filtered using Whatman filter paper and the residue was dried naturally. The pre-treated graphite was added into concentrated H_2SO_4 (300 mL), followed by the addition of potassium permanganate, KMnO_4 (35 g) gradually with stirring. The mixture was stirred at 35 °C for 4 h and diluted with 2 L of water by keeping the temperature under 50 °C. Hydrogen peroxide, H_2O_2 (100 mL) was then added to the mixture drop by drop. The solution was then filtered and washed with 1:10 hydrochloric acid, HCl aqueous solution (2 L) followed by deionized water (2 L). The resulting solid was filtered and dried at room temperature.

Reduction of Graphene Oxide

60 mg graphite oxide was dispersed and sonicated in water (50 mL) for 4 h to exfoliate it. The pH of the solution was then adjusted to pH 10. Hydrazine monohydrate (1.2 mL) was added to the solution and it was refluxed for 24 h at 80 °C.

Functionalization of 1-Pyrenebutyric Acid (1-PB) on Reduced Graphene Oxide (RGO)

10 mg of 1-PB and 10 mg of rGO were dispersed in 5 mL of ethanol, sonicated for 1 h stirred mechanically overnight. The resulting solution was filtered, washed with deionized water and dried in oven at 80 °C for 3 h.

Characterization Methods

rGO, 1-PB and 1-PB-rGO were dispersed in deionized water in concentration of 0.1 mg/mL for UV-Vis measurement. The solutions were then scanned from 200 to 400 nm using Thermo Scientific Genesys 10S UV-Vis. Fourier Transform Infrared Spectroscopy (FTIR) measurements were performed by pressing the materials with potassium bromide (KBr) to form pellets. The pellets were scanned in the frequency range of 400–4000 cm^{-1} using Perkin Elmer Spectrum 100.

Electrochemical Studies

The working electrodes were fabricated by mixing the material with carbon black and polyvinylidene fluoride (PVDF) in the ratio of 80:15:5. The mixture was then dispersed in N-methylpyrrolidone (NMP) and stirred overnight. The slurry was thrush coated onto nickel foam and dried in the oven at 80 °C for 12 h. To assemble the coin cell, two identical pieces of the fabricated electrode were sandwiched with a microglass fiber separator (25 μm , Filter Fioroni) and placed inside the coin cell (CR2032, MTI) with 6 M potassium hydroxide (KOH) as the electrolyte.

Cyclic voltammetry was performed at a potential window of -1 – 1 V at various scan rates ranging from 100 to 5 mV/s. Galvanostatic charge-discharge measurements were performed at different current densities for potential window of 0–1 V. Electrochemical impedance spectroscopy (EIS) was carried out at open circuit potential (OCP) for the frequency range of 500 kHz to 10 mHz. The experiments were conducted at room temperature using PARSTAT 2273.

Result and Discussion

Characterization of RGO and 1-PB-RGO

Figure 1 shows the UV-Vis spectra for rGO, 1-PB and 1-PB-rGO. The spectra for rGO exhibits an absorbance band at 266 nm which is the signature peak for rGO that has a maximum at 270 nm. The presence of this peak is due to the electronic $\pi - \pi^*$ transition of the C=C bond. It indicates that the electronic conjugation within the rGO sheets were restored upon reduction with hydrazine. Meanwhile, the 1-PB-rGO spectra exhibits three absorbance bands. An obvious band at 266 nm which represents the presence of rGO and a shoulder peak at 242 nm and a weak peak at 343 nm. The shoulder peak and weak peak are contributed by 1-PB [4].

To further confirm the successful functionalization of 1-PB on rGO, FTIR measurements were also conducted. Characteristic peaks for GO are observed in

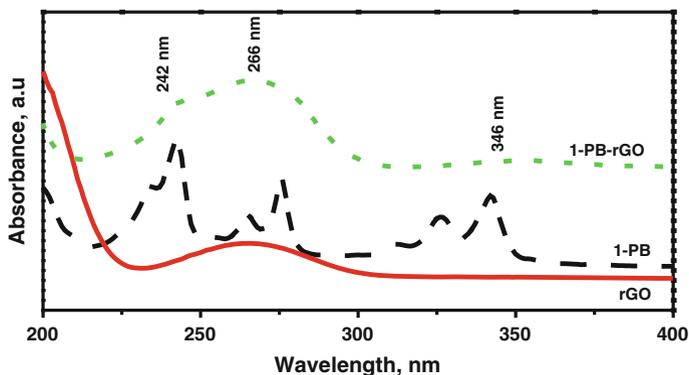


Fig. 1 UV-Vis spectra of rGO, 1-PB and 1-PB-rGO

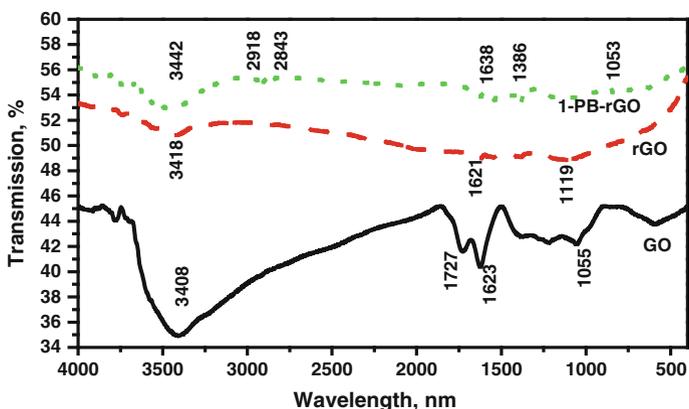


Fig. 2 FTIR spectra of GO, rGO and 1-PB-rGO

FTIR spectrum in Fig. 2 such as the peak due to broad and intense peak contributed by O–H groups at 3408 cm^{-1} , C=O group at 1727 cm^{-1} and C–O stretching at 1055 cm^{-1} . The intense peak contributed by O–H group have diminished significantly as a result of deoxygenation after reduction [6]. For the FTIR spectra of 1-PB-rGO, the signature peaks for rGO at 3442 and 1638 cm^{-1} is observed which is due to O–H group and C=O group respectively. A peak at 1053 cm^{-1} due to C–O stretching is detected too. The peaks contributed by the C–H stretching of alkane at 2918 and 2843 cm^{-1} and C–H rocking of alkane group at 1385 cm^{-1} are also observed. These peaks are most likely due to the functional groups that are present in 1-PB.

Electrochemical Studies

The electrochemical properties of rGO and 1-PB-rGO electrodes were studied using CV, CD and EIS. The specific capacitance for the materials were calculated from the discharge slope using the the following formula:

$$C_{sp}(\text{F/g}) = 4 \times C/m. \quad (1)$$

$$C = I/(dV/dt). \quad (2)$$

where C is the measured capacitance from the two-electrode system and m is the total mass of active materials present in both electrodes. The multiplier 4 is used to adjust the capacitance of the cell and the mass combined from the two electrodes to the capacitance and mass of a single electrode. dV/dt is calculated from the slope of the discharge curve [7].

Figure 3 shows the cyclic voltammogram of rGO and 1-PB-rGO at scan rate of 5 mV/s in 6 M potassium hydroxide (KOH) as the electrolyte. The cyclic voltammogram for rGO yielded an rectangular curve which suggest the idea capacitive behaviour of the rGO [8]. At the same scan rate, the CV curve for 1-PB-rGO is also rectangular in shape with no obvious redox peak. However, the larger area under the curve indicates that the 1-PB-rGO composite possess a better capacitive behaviour.

The galvanostatic charge-discharge study was conducted to observe the sustainability of the capacitive behaviour of the samples studied. Figure 4 shows the galvanostatic charge-discharge curve for rGO and 1-PB-rGO at current density of 0.1 A/g. For both rGO and 1-PB-rGO samples, it can be observed that the charge-discharge curve is triangular in shape which suggest that the charge discharge process is highly symmetrical, leading to ideal capacitive behaviour [9]. The specific capacitance for rGO and 1-PB-rGO were calculated from Eqs. 1 and 2 to be

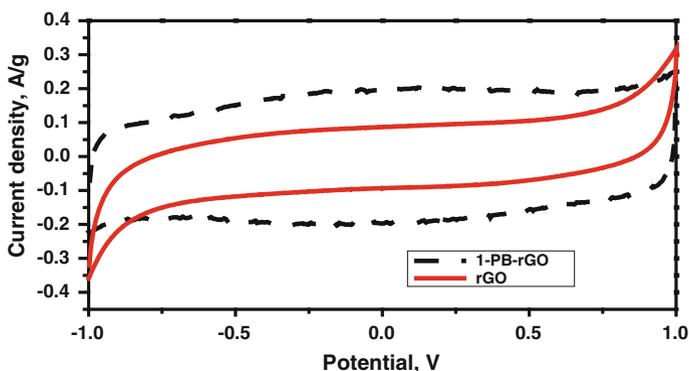


Fig. 3 Cyclic voltammetry (CV) curves for rGO and 1-PB-rGO at scan rate of 5 mV/s

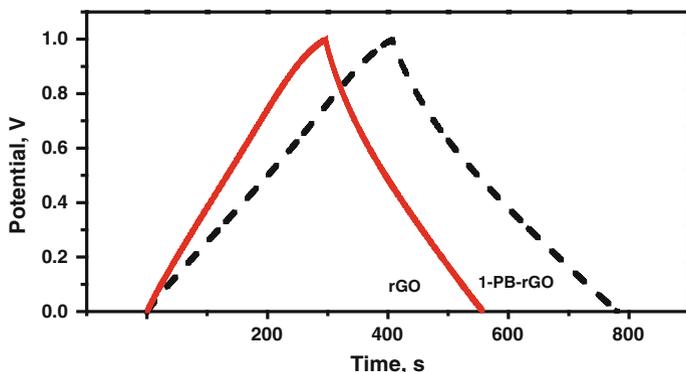


Fig. 4 Galvanostatic charge-discharge curve at current density of 0.1 A/g for rGO and 1-PB-rGO respectively

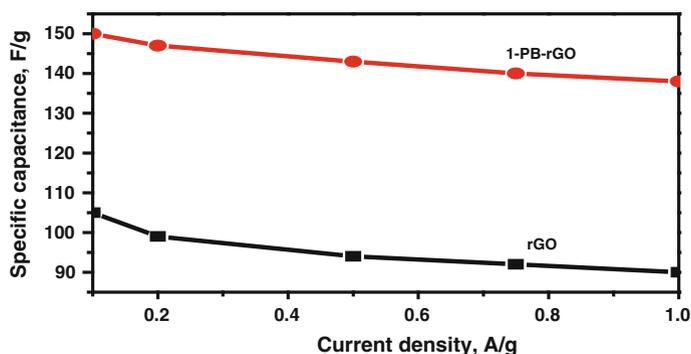


Fig. 5 Plot of specific capacitance of rGO and 1-PB-rGO electrode as a function of discharge current density

105 and 150 F/g (as shown in Fig. 5) respectively. The large enhancement of specific capacitance (approximately 45 %) observed is attributed to the intercalation of pyrene group between the rGO layers which prevented agglomeration of rGO. It is also attributed to the pseudocapacitance contributed by the $-\text{COOH}$ functional group which is attached to the surface of the rGO (Fig. 6).

The electrochemical impedance spectroscopy (EIS) is a powerful tool used in the study of the ion transport at the interface and to probe the resistance limitations present in the supercapacitor fabricated. The intercept of the x-axis of the Nyquist plot at the high frequency end represents the solution resistance (R_s) as illustrated in Fig. 6 [10]. It can be observed from the inset illustration that the R_s is at ~ 0.6 ohm for rGO and ~ 0.5 ohm for 1-PB-rGO. This indicates that the functionalization of rGO with 1-PB improves the R_s of rGO.

This is usually followed by a semi-circular arch which is a representation of the interfacial charge transfer resistance (R_{ct}) and the interfacial capacitance (C_s) which

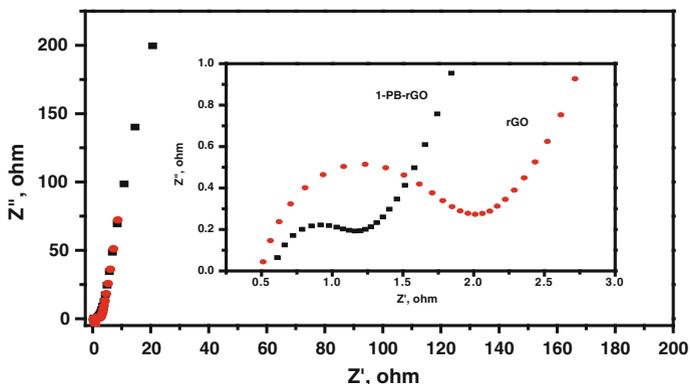


Fig. 6 Nyquist plot for 1-PB-rGO and rGO. Inset shows spectra at high frequency end

are connected at the electrode/electrolyte interface parallelly. The Nyquist plots shows that R_{ct} for 1-PB-rGO is slightly larger than rGO which indicates that some of the pores could be blocked by the 1-PB particles [11]. The last part is the vertical line observed after the semi-circular arch. The slope for rGO and 1-PB-rGO is recorded to be $\sim 83^\circ$ and $\sim 82^\circ$ which shows that the supercapacitor functions closely to an ideal capacitor [10].

Conclusion

This work involves the non-covalent functionalization technique of rGO with 1-pyrenebutyric acid which is simple, cost effective and eco-friendly as it requires only simple sonication and no usage of strong oxidants or corrosive acids. The specific capacitance calculated to be 150 F/g which is an enhancement of 45 % compared to rGO. The enhancement is most probably due to the larger exposed surface area of the material as well as due to the attachment of $-\text{COOH}$ functional group on the surface area of rGO. Therefore, 1-PB-rGO composite is an efficient choice of material to be use in the fabrication of electrode for energy storage application.

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References

1. Ghosh S, An X, Shah R, Rawat D, Dave B, Kar S, Talapatra S (2012) Effect of 1-pyrenecarboxylic acid functionalization of graphene on its capacitive energy storage. *J Phys Chem C* 116:20688–20693
2. Xu Y, Bai H, Lu G, Li S, Shi G (2008) Flexible graphene films via the filtration of water soluble non-covalent functionalized graphene sheets. *J Am Chem Soc* 130:5856–5857

3. Luo L, Zhang Z, Ding Y, Deng D, Zhu X, Wang Z (2013) Label free electrochemical impedance genosensor based on 1-aminopyrene/graphene hybrids. *Nanoscale* 5:5833–5840
4. Li L, Zheng X, Wang J, Sun Q, Wun Q (2013) Solvent exfoliated and functionalized graphene with assistance of supercritical carbon dioxide. *ACS Sustain Chem Eng* 1:144–151
5. An X, Simmons T, Shah R, Wolfe C, Lewis KM, Washington M, Nayak SK, Talapatra S, Kar S (2010) Stable aqueous dispersions of noncovalently functionalized graphene from graphite and their multifunctional high-performance applications. *Nano Lett* 10:4295–4301
6. Choi EY, Han TH, Hong J, Kim JE, Lee SH, Kim HW, Kim SO (2010) Non-covalent functionalization of graphene with end functional polymers. *J Mater Chem* 20:1907–1912
7. Stoller MD, Ruoff RS (2013) Best practice methods for determining an electrode materials performance for ultracapacitor. *Energy Environ Sci* 3:1294–1301
8. Zhu Y, Murali S, Stoller MD, Velamakanni A, Piner RD, Ruoff RS (2010) Microwave assisted exfoliation and reduction of graphite oxide for ultracapacitors. *Carbon* 48:2106–2122
9. Mishra AK, Ramaprabhu S (2011) Functionalized graphene-based nanocomposites for supercapacitor application. *J Phys Chem C* 115:14006–14013
10. Hastak RS, Sivaraman P, Potphode DD, Shashidhara K, Samui AB (2012) All solid supercapacitor based on activated carbon and poly(2,5-benzimidazole) for high temperature application. *Electrochim Acta* 59:296–303
11. Su Y, Zhitomirsky I (2013) Electrophoretic assembly of organic molecules and composites for electrochemical supercapacitors. *J Colloid Interface Sci* 392:247–255