

Covalent Grafting of N-Containing Compound with Graphene Oxide: Efficient Electrode Material for Supercapacitor

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Abstract: Metal free N-containing compounds grafted graphene oxide (GO) composites have played crucial role in energy storage applications. In this work, covalent functionalization of graphene oxide (GO) with diethylenetriamine (DETA) was achieved by a simple addition reaction. Various spectroscopic and microscopic techniques such as X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FT-IR), X-ray powder diffraction (XRD), Raman and thermogravimetric analysis (TGA) were performed to confirm the structure of the resultant GO/DETA. Results confirmed that the GO/DETA have N-rich group on the surface of GO. Cyclic voltammetry, galvanostatic charge-discharge and electrochemical impedance spectroscopy were carried out for GO and GO/DETA. The functionalized GO material, GO/DETA, showed superior capacitive behaviour of 255 F/g in 6 M KOH at 10 mV s⁻¹ when compared to fresh GO (136 F/g). The specific capacitance retention value of GO/DETA was found to be 92%, revealed high stability of GO/DETA.

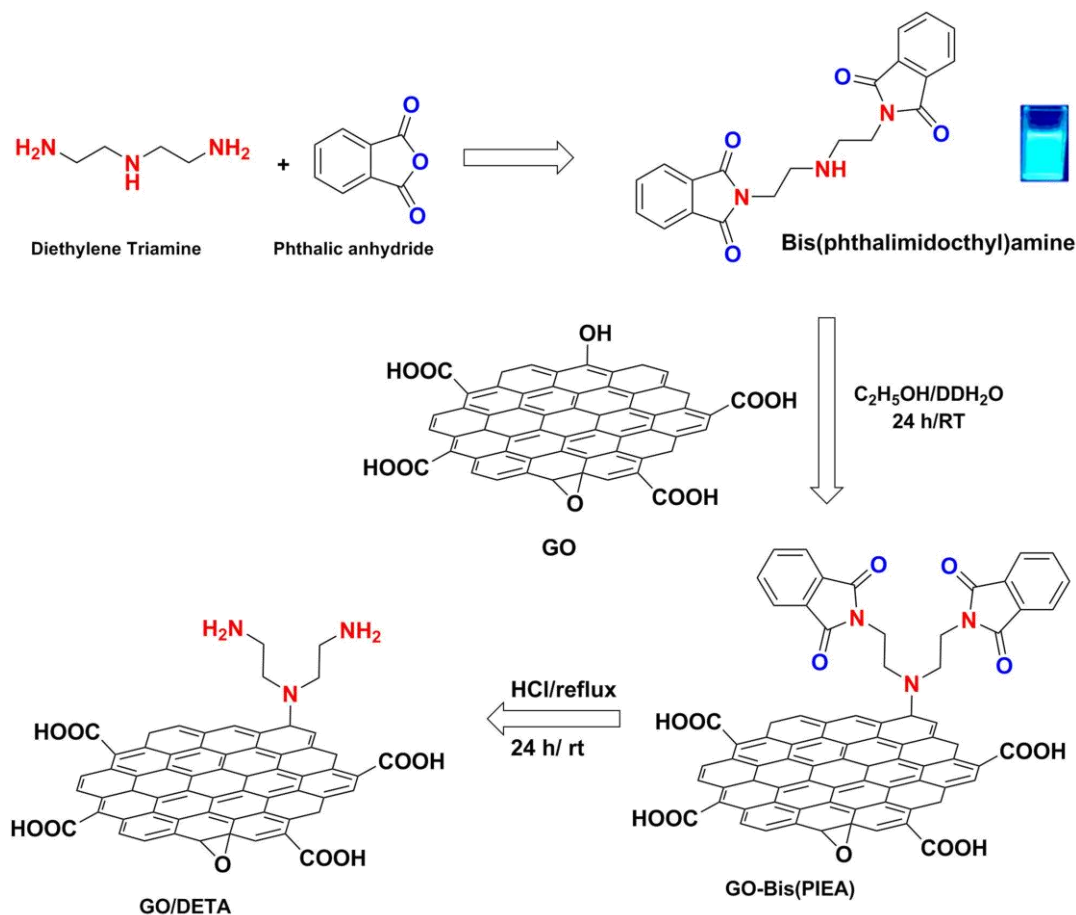
Keywords: Graphene oxide; diethylene triamine; covalent functionalization; supercapacitor; stability

1. Introduction

Capacitive performance of carbon materials is mostly depending on their surface area, pore geometry, electrical conductivity and chemical environment.^[1] The surface modification of carbon matrix with O, N or P contained functional groups could possible improve the capacitance effects of the electrodes. In fact, the functional groups on the carbon surface can facilitate a better wettability.^[2] The covalent grafting of polymers with GO surface was successfully carried out by Li and co-workers.^[3] Alike, polymer-GO interactions are well studied by means of various spectral and analytical studies.^[4] The surface modification of GO with various organic/inorganic moieties was demonstrated to be an efficient route to transform the electrode material highly suitable for supercapacitor application.^[5,6] Furthermore, GO has more amount of sp³ hybridized carbon, thus, possesses substantial band gap, which is obviously important factor in achieving unique grafted GO composites.^[7] N-Containing moieties (example, triethanolamine,^[8] diamino pyridine^[9] and so on) are often used to covalently functionalize the GO *via* grafting method. The functional groups based on heteroatom enhance the wettability and capacitance properties of porous carbon materials. Unfortunately,

the usefulness of such composites is very limited. The epoxy functional groups present in GO has an intrinsic pathway to counter with an electron-donating functional group sowing to its difference in electronegativity.^[10] Thus favours GO to undergo nucleophilic substitution reaction with amino/imino moieties even at mild reaction conditions. Joon Oh and coworkers^[11] reported pulsed flash-light irradiated GO thin film as electrode material for supercapacitor and the specific capacitance of 220 F g⁻¹ at the scan of 5 mV s⁻¹ in 6M KOH was achieved. Similarly, Song et al.^[12] used triethanolamine-functionalized GO as electrode material and the capacitance of 211 Fg⁻¹ in 1M H₂SO₄ was achieved.^[13] Sun et al.^[14] have investigated the N-incorporated GO electrode materials by hydrothermal process. Further, the materials obtained the superior capacitance of 265 Fg⁻¹ in 6M KOH was achieved and maintained at 89.8% of capacitance even after 5000 charge and discharge cycles.

Graphene oxide can be covalently modified by functional groups that contain heteroatom such as fluorine, nitrogen, and oxygen.^[15] The unique morphology and textural properties are the key advantages of the covalently grafted GO.^[12, 16-19] Particularly, grafting organic molecules on GO could lead to the additional aromatic character, resulting in change of electronic properties.^[20,21]



Scheme 1. Schematic diagram for the preparation of GO/DETA.

Furthermore, covalent approaches offers excessive benefit of attaining long-lasting stabilization of the isolated graphene sheets.^[22] In fact, the functionalization could improve the properties of GO such as surface charge, wettability and electron mobility.^[23,24] In our previous project,^[25] bis(phthalimidoethyl)-amine grafted GO composites was prepared by a facile synthetic route. In the present study, GO grafted diethylenetriamine (GO/DETA) was obtained from the above GO/bis(phthalimidoethyl)-amine by a simple HCl treatment. We believed that the additional free NH₂ groups on the GO surface would show interesting result in the energy storage applications (example: better conjugation, wettability, inter-layers spacing). The prepared GO/DETA was characterized by Raman, FT-IR, XPS, XRD, TGA and HRTEM-SAED. Cyclic voltammetry curves were recorded for GO and GO/DETA. Similarly, electrochemical impedance spectroscopy (EIS) and galvanostatic charge-discharge (GCD) were carried out for GO and GO/DETA

2. Experimental Section

2.1. Materials

Graphite oxide (GO, 500 mesh) was received from Sigma-Aldrich, USA, Conc. H₂SO₄, sodium metaperiodate, ethanol, THF and 30% aqueous H₂O₂ were acquired from Sigma-Aldrich. Diethylenetriamine (DETA) and phthalic anhydride was purchased from Merck (India). All the used reagents were analytical grade and used as it is.

2.2. Synthesis of graphene oxide

Hummer's method was adopted for the generation of GO from graphite oxide powder. In a typical reaction, a mixture of 1 g of graphite powder and 40 mL of Conc. H₂SO₄ (98.5%) was stirred at 27°C for 30 min and then subjected to ultra-sonication process for 60 min. After cooling down to 0°C, 12 g of sodium metaperiodate was introduced to the mixture and stirred vigorously for 24 h. The mixture (thick, grey colour paste) was diluted slowly with 150 mL of distilled water with continuous stirring. It was observed that upon the addition of distilled water, the grey colour reaction mixture turns into dark brown colour. To the above mixture, 5 ml of 30% H₂O₂ was added and stirred for 1 h and centrifuged. The solid GO was washed with 1:1 (v/v) aqueous ethanol (2x 20 ml) and diethyl ether (20 ml), finally, the dark brown product was dried and stored in the desiccators.

2.3. Preparation of GO/DETA

The GO/DETA was prepared *via* three simple steps. At first, bis(phthalimidoethyl)-amine was synthesized by using phthalic anhydride and DETA. Briefly, a 5.7g (0.038 M) of phthalic anhydride was heated at 120°C for 30 min with continuous stirring and then 2.1 ml (0.019 M) of DETA was slowly added. To the above residue, 100 ml of ethanol was added and stirred for 2 h. The isolated yield of bis(phthalimidoethyl)-amine was calculated to be 94% (6.8 g).

To further, bis(phthalimidoethyl)-amine was used for the preparation of GO/bis(PIEA). Typically, 500 mg of GO was dispersed in 150 ml of DI water and then subjected to sonication process for 30 min. To the above mixture, 1 gm of bis(PIEA) dissolved ethanol was introduced slowly under continuous stirring for 24 h. Finally, the mixture was centrifuged at 5000 rpm for 10 min to isolate the GO/bis(PIEA). The black GO/bis(PIEA) solid was washed with ethanol and diethyl ether.

In the typical preparation of GO/DETA, 300 mg of GO/(Bis(PIEA) treated with 10% HCl solution under reflux condition for 24h. The GO/DETA was isolated by centrifugation of the above mixture at 5000 rpm for 10 min. Alike GO/bis(PIEA) solid, the resultant GO/DETA was washed well with hot water, ethanol and diethyl ether.

2.4. Characterization

FT-IR (IR Prestise-21 Shimadzu), XRD (Shimadzu XRD-6000 Powder X-Ray diffractometer) patterns were recorded for both GO and GO/DETA. For the XRD analysis, 40 kV voltage and 30 mA current were applied. High-resolution TEM and selected area electron diffraction (HR-TEM and SAED) were performed on a JEOL JEM-2100. Raman spectra were logged on a Horiba-Jobin Raman spectrometer. X-ray photoemission spectroscopy (XPS, XPS instrument (Carl Zeiss)) was performed for fresh GO and GO/DETA. TGA analysis was performed under a N₂ atmosphere by means of NETZSCH STA 449 F3 Jupiter.

3. Results and Discussions

3.1. Characterization of GO and GO/DETA

The covalent functionalization of DETA with GO was performed in three steps (Scheme 1). At first, DETA and phthalic anhydride were reacted to form bis(phthalimidoethyl)amine. In the second step, GO was reacted with bis(phthalimidoethyl)amine to obtain GO/bis(PIEA). Finally, in the third step, hydrolysis of GO/bis(PIEA) by refluxing it with 20% of hydrochloric acid was achieved and GO/DETA was

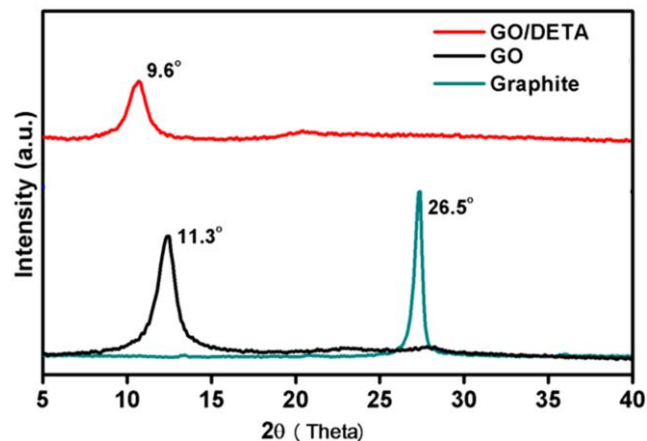


Fig. 1. XRD patterns of graphite, GO and GO/DETA.

obtained. The resultant GO/DETA black precipitate was obtained after centrifugation process and then subjected to washing process with hot water and ethanol.

Fig. 1 demonstrates the XRD patterns of graphite, GO and GO/DETA. The crystallinity structure and the interlayer d-spacing of GO/DETA were investigated. The XRD pattern of graphite showed peak at 26.5° whereas after oxidation process the GO showed a strong peak at 2θ = 11.2° with an interlayer separation of 0.78 nm. This is mainly due to the existence of plentiful O₂⁻ containing groups and H₂O molecules on the surface of GO. The XRD data for the GO/DETA material diffraction peaks at 2θ value is 9.6° with the d-spacing of 0.9 nm. Afterwards, the increase in interlayer d-spacing from 0.78 to 0.9 nm is mainly due to the intercalation of DETA covalently onto the surface of GO. It could be higher for GO/bis(PIEA) since it has bulky molecules in its structure. The full width of half maximum (FWHM) value of the diffraction peak in the XRD pattern of GO/DETA was found to be higher when compared to that of GO. To further, average crystallites thickness of the GO/DETA was also estimated using the Debye-Scherrer equation.^[13,26] (Equation 1)

$$T = K\lambda / \text{FWHM} \cos \theta \quad (1)$$

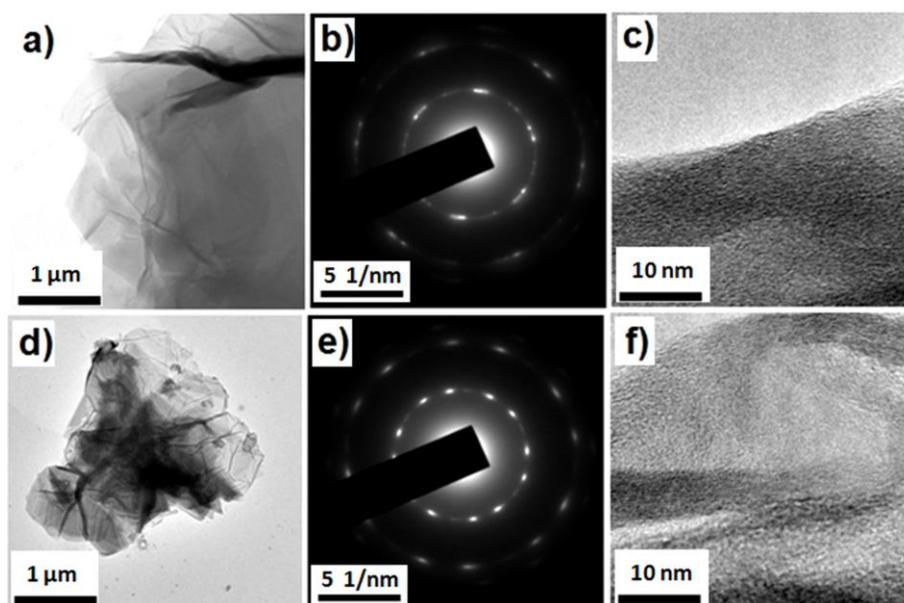


Fig. 2. TEM images of (a, c) GO and (d, f) GO/DETA. SAED patterns of (b) GO and (e) GO/DETA.

where t – average crystallites thickness, K is a dimensionless shape factor with a value of about 0.9, λ - wavelength of X-ray used (λ -1.5418), and θ - angular position of the peak. The T -values of $\sim 71\text{\AA}$ and 47\AA were determined for GO and GO/DETA, respectively. Equation (2) was applied to calculate the number of layers (N).

$$N = t/d \quad (2)$$

Whereas t represents average crystallites thickness and d represents lattice spacing and N represents number of layers (5 for functionalized GO/DETA).^[27]

The HR-TEM images and SAED patterns of GO and GO/DETA are presented in Fig. 2. The SAED patterns of GO (Fig. 2b) confirmed the crystalline nature of the GO sheets. The lamellar morphology of the GO/DETA can be seen in the HR-TEM images (Fig. 2f). It can be seen that both materials (GO and GO/DETA) have more wrinkles and crumples in its morphology, which confirm the regeneration of few layers of the GO-composite. In addition, the presence of carbon layers in GO/DETA is mainly due to the presence of numerous lattice fringes supporting the previous claim. The obtained results are in good consistent with the XRD results. Moreover, the SAED pattern of GO/DETA is displayed in the Fig. 2(e and h). Well-defined diffraction spots were noted for the GO/DETA which indicates DETA intercalation on the surface of GO.^[25,28] Moreover, the GO/DETA was found to be nano-crystalline in nature.

The as-prepared GO and GO/DETA were further confirmed by FT-IR analysis (Fig. 3). GO showed distinctive peaks at 3436 , 1755 , 1630 and 1028 cm^{-1} equivalent to hydroxyl (-OH), carbonyl (C=O), aromatic ring (C=C) and epoxy (C-O) stretching vibrations, respectively. Similarly, the FT-IR spectrum of GO/DETA validates new peaks at 1703 , 1579 , 1381 , 1185 and 1049 cm^{-1} agreeing to amide C=O, aromatic (C=C), hydroxyl(-OH) bending, and C-N and C-O stretching vibrations, correspondingly. In addition, the broad peak at 3374 cm^{-1} is credited to -OH group. This results confirms that the covalent functionalization of DETA with GO.^[29,30]

The Raman spectra of GO and GO/DETA are shown in Fig. 4. The Raman spectrum of GO shows two dominant G band and D band at

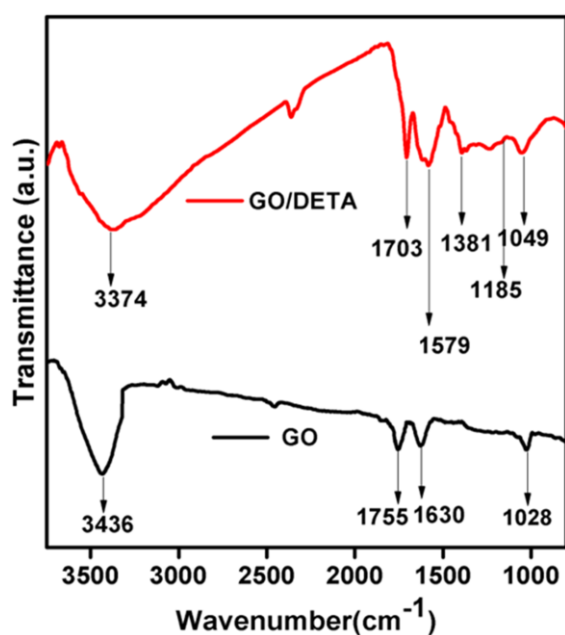


Fig. 3. FT-IR spectra of GO and GO/DETA.

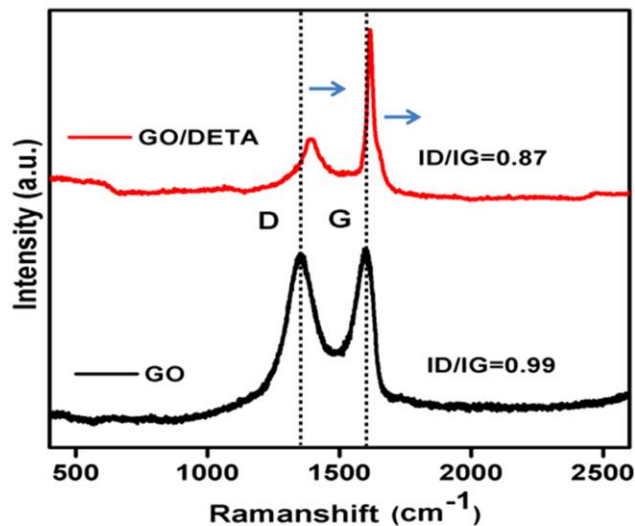


Fig. 4. Raman spectra of GO, and GO/DETA.

1593 cm^{-1} and 1349 cm^{-1} respectively. However, after functionalization, the Raman spectrum of GO/DETA showed shift in the G-band (from 1593 cm^{-1} to 1575 cm^{-1}) and D-band (from 1349 cm^{-1} to 1340 cm^{-1}). This phenomenon is mainly due to the formation of the structural defects *via* functionalization of DETA with GO.^[31] The calculated ID/IG ratio of GO is 0.99, whereas, the GO/DETA showed about 0.87. The decrease in the ID/IG ratio shows the regeneration of sp^2 -carbon domains *via* the covalent functionalization of DETA with GO.^[32,33]

The thermal stability of the GO and GO/DETA was examined by TGA (Fig. 5). According to the previous literature, the weight loss of GO between 190 - 230°C is mainly credited to the elimination of liable oxygen groups and H_2O . Above 250°C , the most stable groups such as -OH, quinone and terminal carboxyl undergoes complete degradation. For GO/DETA, there is a slight weight loss of 10-15% at 250°C due to the removal of labile O_2 -containing moieties on the carbon surface. Further, the sluggish degradation was detected above 250°C and about 30% of mass loss was noted due to the decomposition of amino-carbons. The better thermal stability of GO/DETA when compared to GO indicates the efficient covalent intercalation by free amino groups during the functionalization of GO.^[34]

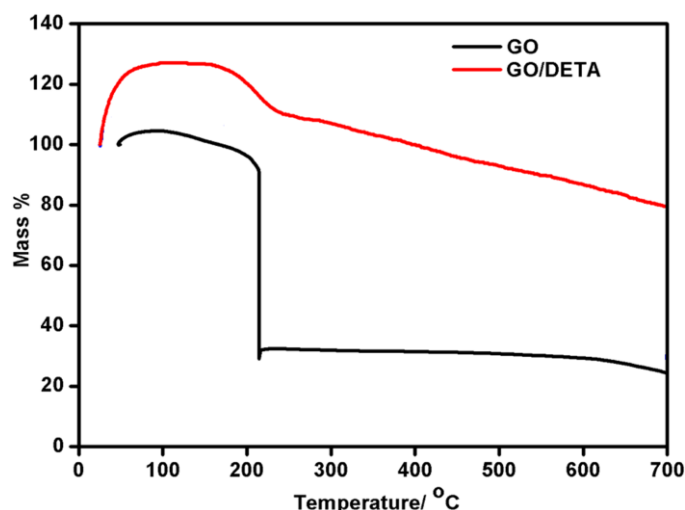


Fig. 5. TGA curves of GO and GO/DETA.

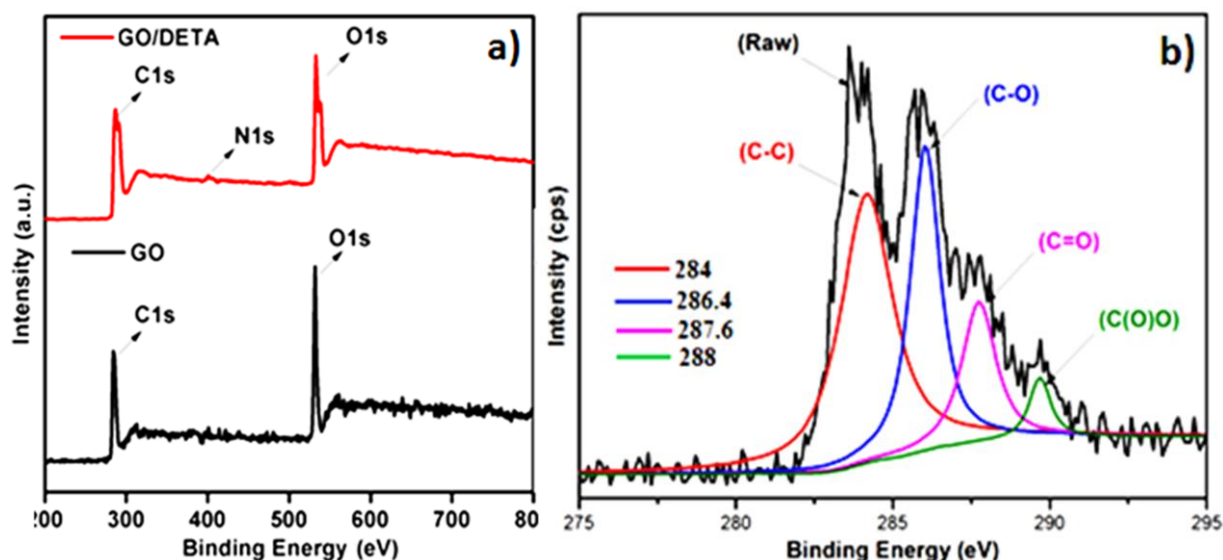


Fig. 6. (a) XPS survey spectra of GO and GO/DETA, and (b) deconvoluted C 1s XPS peak of GO.

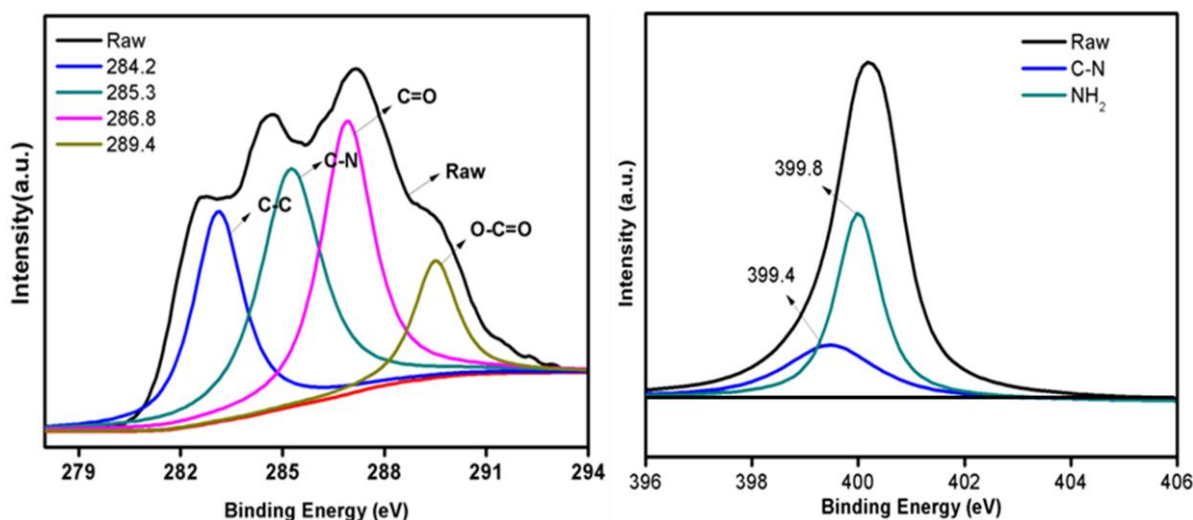


Fig. 7. Deconvoluted C 1s and N 1s XPS peaks of GO/DETA.

The chemical nature of the GO and GO/DETA was investigated by XPS (Fig. 6 and Fig. 7). Both GO and GO/DETA showed two dominant peaks C 1s and O 1s at ~285 and 534 eV respectively.^[35] The fitting of C 1s XPS spectrum of GO resulted in four peaks at 284 (C-C), 286.4 (C-O), 287.6 (C=O (epoxide and hydroxyl)) and 288 eV (O-C=O, carboxyl groups). However, the XPS spectrum of GO/DETA shows a new peak at 400.2 eV agrees to N 1s, indicating the successful functionalization of amine on the GO surface. The peak fitting of C1s and N1s was performed to study the various carbon and nitrogen components functionalized GO surface. Moreover, the deconvoluted C 1s XPS spectrum of GO/DETA (Fig. 7) confirmed the existence of four different types of functional groups on the surface of GO. The peak at 284.2 eV is typically attributed to the graphitic C-C bond, while, the binding energies at 285.3 and 286.8 eV are originated from C-N and C-O bonds, correspondingly. In addition, the presence of terminal C=O group in GO/DETA was confirmed by observing a strong peak at 289.4 eV.^[29] The results confirmed the existence of C-N bonds and abundant O₂-functional groups in GO/DETA.^[36,37]

3.2. Electrochemical performance of GO and GO/DETA

The electrochemical behaviour of GO and GO/DETA is performed by CV, GCD and EIS techniques. The working electrode was prepared by coating the GO/DETA or GO over glassy carbon electrode and the electrochemical measurements were performed in 6M KOH electrolytic solution. In order to eliminate excess dissolved oxygen, the three electrode system was initially kept under N₂ atmosphere. The CV curves of GO and GO/DETA at various scan rates in the range of 10 to 100 mV/s vs Hg/HgCl are shown in Fig. 8. The potential window of -0.8 to 0.6 V was chosen. The rectangular shape of CV curves of GO/DETA guarantee an ideal capacitive behaviour of the present material.^[38,39]

The CV plots of GO and GO/DETA at numerous scan rates confirm that there is no faradic reaction happens at the electrode surface, indicating the perfect capacitive nature of the present materials. Upon increasing the scan rates, the CV curves proportionally enlarged and does not show any significant redox peaks. However, a hump type increase can be noted during the larger number of cycles, indicating the distinctive redox nature of the present electrodes. It

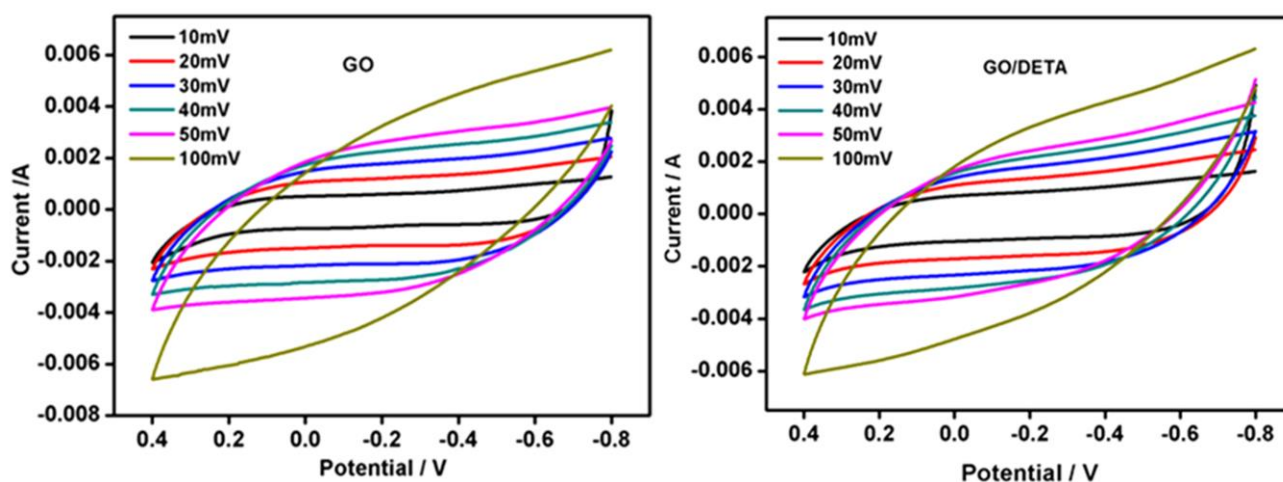


Fig. 8. Electrochemical performances of GO and GO/DETA at 10 mV s⁻¹ in 6 M KOH at different scan rates.

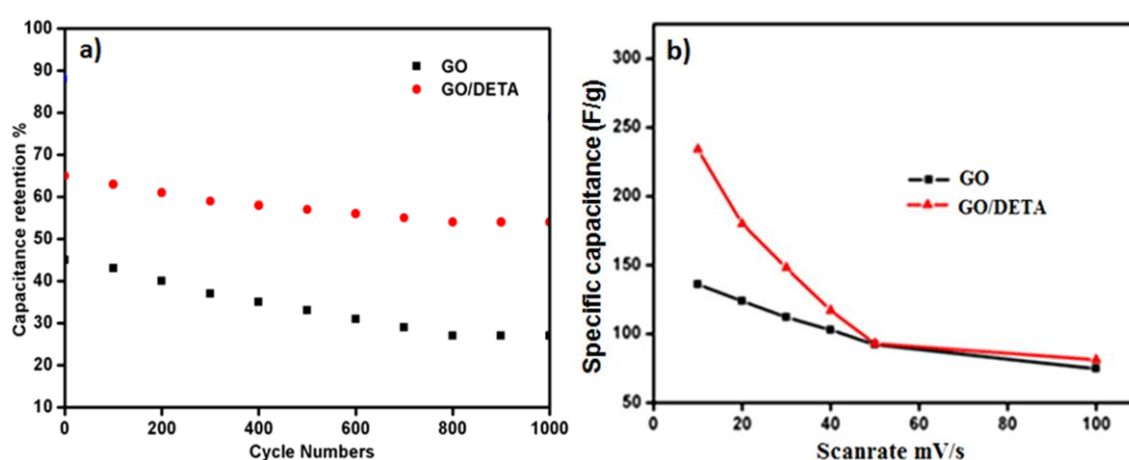


Fig. 9. (a) Capacitance retention of GO and GO/DETA. (b) Rate-dependent plot of the specific capacitance values of GO and GO/DETA.

can be concluded that the capacitance nature of GO/DETA is mainly by electrode double layer capacitance (EDCL) type rather than pseudocapacitance.^[40] The EDLC is mainly due to the electrostatic interface interactions between GO/DETA and electrolyte. Moreover, the charge accumulation at the surface of electrodes depends on the applied bias and available surface functional groups. The attendance of amino-groups strongly prevents the graphene layers from the face-to-face aggregation (higher *d*-spacing) which assists for the complete exploitation GO surface. In addition, the covalent interaction between N-atoms and graphene matrix donates electrons to the GO aromatic rings and therefore enhancing the capacitance of GO/DETA in comparison to the fresh GO. The stability of GO and GO/DETA was investigated. The CV analysis was repeated at scan rate of 100 mV s⁻¹ for 1000 cycles at the current density of 1 A g⁻¹. As evidenced from the Fig. 9a, the capacitance retention values are found to be very good, 92% for GO/DETA.

3.3. Galvanostatic charge–discharge curves

The GCD curves of GO and GO/DETA materials were tested under controlled conditions. The specific capacitance and long-term stability were determined for both GO and GO/DETA. Equation 3 was used to calculate the specific capacitance of GO and GO/DETA.

$$C_s = \frac{I \times \Delta t}{m \times \Delta v} \quad (3)$$

Where, C_s , I , Δt , Δv and m represents specific capacitance (F/g), discharge current (A), discharge time (s), potential difference (V) and mass of the GO or GO/DETA (g), respectively. The charge/discharge experiments are carried out in the voltage range of zero to 0.4 V at the constant current density of 1 A g⁻¹ (Fig. 10a). The calculated specific capacitance of GO/DETA and GO electrode were 255 and 136 F g⁻¹ respectively, which shows about 1.5-fold higher C_s value of GO/DETA when compared to fresh GO (Fig. 10a). The better C_s value of GO/DETA is mainly due to the three key points; (a) easy access of electrolyte to the inter-layer pores of the active material, (b) excellent wetness, and (c) covalent functionalization of DETA with GO.^[28,31]

The impedance spectra were recorded for GO, GO/bis(PIEA) and GO/DETA at the open circuit voltage potential over the frequency varied from 1Hz to 100 kHz. Further, the amplitude and initial voltage is maintained at 0.001V and 0.4V, respectively. EIS plots are analysed using Nyquist plots of GO/bis(PIEA), GO/DETA and GO materials (Fig. 10b), which indicate the frequency responsive of the elevated electrolytic system. In particular, the obtained Nyquist plots show

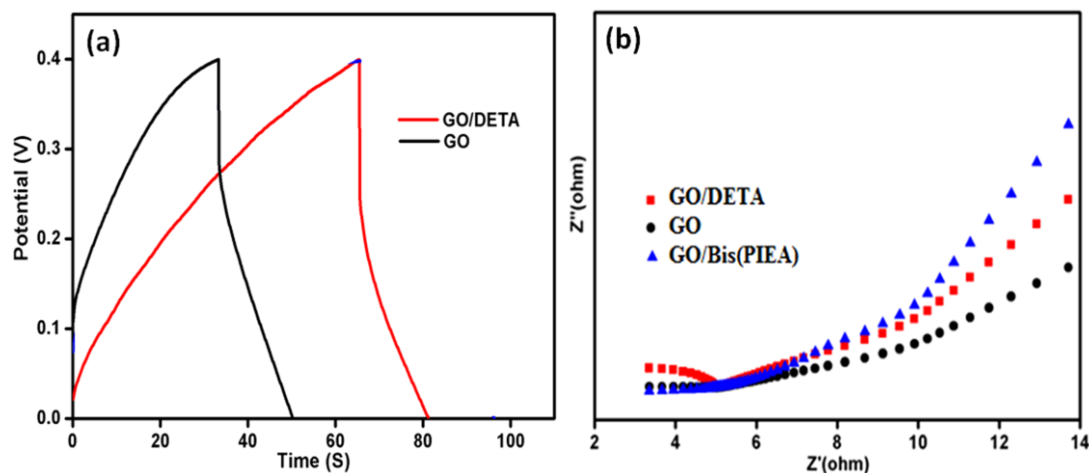


Fig. 10. (a) Galvanostatic charge–discharge curves of GO and GO/DETA electrode at the current density 1 A g^{-1} . (b) AC impedance Nyquist plot of GO, GO/bis(PIEA) and GO/DETA materials.

two regions including a semicircle in high frequency region and a vertical line in the low frequency region. In case of fresh GO, the high frequency half arc is reasonably small, which illustrates that the electrode/electrolyte interface charge transfer resistance is quiet low in the electrode materials (Fig. 10b). The Nyquist plots of GO/DETA show an oblique line instead of the theoretically-assumed vertical line relative to the axis, indicating the better ion diffusion across the electrolyte-to-electrode interface and the surface layers of the electrochemically active materials.^[41,42]

4. Conclusions

Diethylenetriamine (DETA) grafted GO (GO/DETA) was successfully obtained via simple covalent functionalization. Numerous spectroscopic and microscopic techniques such as XPS, TEM, FT-IR, XRD, Raman and TGA were performed to confirm the structure of the resultant GO/DETA. Results confirmed that the GO/DETA have N-rich group on the surface of GO. CV, GCD and EIS measurements were performed for GO and GO/DETA. The functionalized GO material, GO/DETA, showed superior capacitive behaviour of 255 F/g in 6 M KOH at 10 mV s^{-1} when compared to fresh GO (136 F/g). The specific capacitance retention value of GO/DETA was found to be 92%, revealed high stability of GO/DETA. The functionalized GO based energy materials will have incredible potential usage in the arena of energy storage applications.

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Conflicts of Interest

The authors declare no conflict of interest.

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