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ARTICLE

In situ preparation of SAC-RGO@Ni electrode by electrochemical functionalization of reduced graphene oxide using sulfanilic acid azocromotrop and its application in Asymmetric supercapacitor

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In-situ electro-deposition, reduction and functionalization of graphene oxide (GO) with sulfanilic acid azocromotrop (SAC) was carried out through a facile one-step electrochemical method. The nickel foam was used as the anode during the electro-deposition and the aqueous solution of SAC along with GO was used as the electrolyte. The SAC modified reduced GO (RGO) deposited on the nickel foam (SAC-RGO@Ni) and was directly used as the electrode for capacitive property analysis. The reduction and functionalization of GO was examined by Fourier transform infrared (FT-IR), Raman and X-ray photoelectron spectroscopy (XPS) techniques. The SAC-RGO@Ni provides very high specific capacitance of $\sim 1090 \text{ F g}^{-1}$ due to the synergistic effect of double layer capacitance of RGO and the pseudocapacitance of $-\text{SO}_3\text{H}$ functionalities of SAC. The asymmetric supercapacitor (ASC) cell was designed with SAC-RGO@Ni and thermally reduced GO (TRGO) as positive and negative electrode, respectively. The ASC device exhibits high effective capacitance of $\sim 495 \text{ F g}^{-1}$ at a current density of 10 A g^{-1} and $\sim 93\%$ of its total discharging time lies in between 1.5 to 0.75 V. The ASC cell remains stable up to 10,000 charge-discharge cycles. Furthermore, the SAC-RGO@Ni-based ASC device can provide very high energy density of $\sim 88.9 \text{ W h Kg}^{-1}$ and large power density of $16,500 \text{ W Kg}^{-1}$ ensuring its applicability in high power consumable devices.

1. Introduction

High power density, fast rates of charge-discharge, and excellent cycling stability are the desirable characteristics of the new generation energy storage devices to support the portable electronics and electric vehicles.¹⁻⁴ However, for the practical application of the electronic devices requires the improvement in energy density of supercapacitor without affecting its power density or stability.^{2,3} Therefore, the best way is to utilize the asymmetric configuration with different cathode and anode materials as the energy density is directly related to the potential window.^{2,5,6} The asymmetric supercapacitor (ASC) has enhanced operating voltage (larger than 1.2 even in aqueous solution) and at the same time can use both electric double layer as well as pseudo electrode as positive and negative electrode materials, respectively.^{5,7,8} The carbonaceous materials like thermally reduced graphene

oxide (GO), hydrothermally reduced GO, carbon nanotube or activated carbon are well established negative electrode materials with perfect EDLC nature.^{1,9} Generally, the materials with pseudo nature are used as the positive electrode materials. Graphene-based composite materials are the perfect choice that can provide the combination of faradaic and non-faradaic charge storage mechanism during charge discharge cycle.^{1,2,9} Furthermore, different covalent and non covalent surface modification of reduced GO (RGO) can provide the pseudo capacitance along with the EDLC.¹⁰ The advantage of using the surface treated RGO as compared to the metal oxides is the high electrical conductivity.^{1,2,7,10-13} The surface modification also prevents the restacking of graphene layers and increase the effective surface area providing good ionic exchange with electrolyte.^{10,13} Among the few materials with single atomic sheet, graphene is very useful for fundamental as well as application oriented research due to its remarkable mechanical, electrical and optical properties.^{1,9} Apart from the different techniques for graphene synthesis, the reduction of GO is the easiest and cost-effective method.^{1,10} GO, which is a highly oxidized form of graphene, can be synthesized from graphite flake through well known Hummer's method.^{10,12,13} The presence of polar organic groups, including carboxylic acid, epoxy, phenol, and aldehyde functional groups make GO poor conductor of electricity.^{13,14}

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But at the same time GO is highly hydrophilic so that it is possible to disperse it easily in aqueous solvent.¹⁴

There are different approaches such as thermal reduction, flash reduction, enzymatic reduction, but the most common is heating in reducing atmospheres with different reducing agent like ammonia, hydrazine or urea.^{13,14,15} Though, there is a few reports on the electro-deposition of graphene, but, it may be a potential, simple and cost effective method for future applications.^{13,16} Extremely controllable, conformal films of RGO can be formed without using any volatile solvents or reducing agents.¹⁴ Shao et al. and Gilje et al. have reported two-step method: at first the pre-applying GO dispersions directly onto the electrode followed by the reduction of GO in presence of electrolyte.^{16,17} Ramesha et al. and Wang et al. have shown that the functionalization of GO coated electrode can achieve improved electrical and electrochemical properties.^{18,19} Hilder and his co-workers have demonstrated simultaneous anodic electro-deposition and reduction of GO rather than the post-reduction of pre-coated electrode.¹⁴ Sodium 4-aminoazobenzene-4-sulfonate modified graphene can be used as supercapacitor electrode material and showed the specific capacitance of $\sim 210 \text{ F g}^{-1}$.²⁰ Jaidev and his co-authors have reported poly (p-phenylenediamine) modified graphene electrode material with a specific capacitance of $\sim 248 \text{ F g}^{-1}$ at a current density of 2 A g^{-1} .²¹ Kumar et al. have shown the application of poly(3,4-propylenedioxythiophene) as a surface modifying agent and the modified GO electrode exhibited a specific capacitance of 201 F g^{-1} at a scan rate of 10 mV s^{-1} .²² Jana et al. have reported the preparation of sulfanilic acid azocromotrop (SAC) modified RGO (SAC-RGO) and the synthesised material exhibited relatively high specific capacitance of 366 F g^{-1} .¹⁰ The SAC-RGO was prepared by non-covalent functionalization of GO followed by the reduction using hydrazine monohydrate.¹⁰ The SAC was embedded on the surface of graphene through π - π interaction.¹⁰ The $-\text{SO}_3\text{H}$ functional groups of SAC can provide additional faradic charge storage mechanism due to the surface compatibility with the aqueous electrolyte along with the EDLC of graphene when used as the electrode materials.

Herein, one-step electro-deposition method for the functionalization as well as reduction of GO from the aqueous dispersion has been demonstrated. Conducting nickel foam was used as the electrodes and the anode was directly used in the supercapacitor applications. Electro-deposition of graphene layers on the positive electrode is expected due to the presence of electrically negative functional groups on the surface of GO. At the same time, electrically negative $-\text{SO}_3\text{H}$ functional groups will also deposited on the positive electrode. Thus, SAC embedded graphene layers on the nickel foam are expected due to the π - π interaction. The electrochemical performances of the as synthesised nickel foam were studied in three electrode method. The ASC device was also fabricated by using the electrodeposited nickel foam as positive electrode and the thermally reduced GO as the negative electrode.

2. Experimental

2.1 Materials

Natural flake graphite, Polyvinylidene fluoride (PVDF) and sulfanilic acid azochromotrop (SAC) were purchased from Sigma-Aldrich. Sulphuric acid, hydrogen peroxide, potassium permanganate and N,N-dimethyle formamide (DMF) were obtained from Merck, Mumbai, India. Conducting carbon black (EC-600JD, purity: $>95\%$) was purchased from MTI Corporation, USA. Nickel foam was purchased from Shanghai Winfay New Material Co., Ltd., China.

2.2 Preparation of SAC-RGO@Ni

GO was prepared according to modified Hummer's method.¹⁰ The electrolyte was prepared by dissolving $\sim 100 \text{ mg}$ of GO and $\sim 300 \text{ mg}$ of SAC in 100 ml distilled water. Two pieces of nickel foams ($2 \text{ cm} \times 5 \text{ cm}$) were taken as the electrode. About 0.04 A current flow was maintained for ~ 30 minutes. The deposited anode (SAC-RGO@Ni) was collected, washed with distilled water and dried at 60°C for $\sim 24 \text{ h}$. The RGO@Ni was prepared by using the aqueous dispersion of GO as electrolyte. In order to carry out the controlled experiment, the SAC@Ni electrode was prepared using only SAC solution as electrolyte.

2.3 Structural and morphological characterization

The details about the sample preparation for different characterization and property analysis have been discussed in the supporting information. Fourier transform infrared spectra (FT-IR) of pure GO and SACRGO were recorded with Perkin Elmer, Spectrum 100. X-ray diffraction (XRD) studies of the composite were carried out at room temperature on a PANalytical High Resolution XRD-I, PW 3040/60 at a scan rate of 1° min^{-1} (Cu K α radiation, $\lambda=0.15418 \text{ nm}$). Field emission scanning electron microscopy (FE-SEM) images were recorded with Sigma HD, Carl Zeiss, Germany. Raman spectra of the samples were obtained on a Nano-finder 30 (Tokyo Instruments Co., Osaka, Japan) using a laser wavelength of 514 nm and a 100 mm spot size. X-ray photoelectron spectroscopy (XPS) of SAC-RGO was carried out with PHI 5000 Versa Probe II (ULVAC-PHI, Inc, Japan) using monochromatic Al K α source ($h\nu = 1,486.6 \text{ eV}$). The defect content of SAC-RGO was measured by Raman spectrometry (T64000), Jobin Yvon Horiba, France. Transmission electron microscopy (TEM) images were recorded with JEOL JEM-2100 FS.

2.4 Electrical and electrochemical properties

The electrical conductivity was measured using a four probe set up with a KEITHLEY delta system consisting of an AC and DC current source (model: 6221) and a Nanovoltmeter (model: 2182A).

Electrochemical measurements were carried out with PARSTAT 4000 (Princeton Applied Research, USA) in both three and two

electrode configuration. The cyclic voltammetry (CV), galvanostatic charge-discharge (CD) and electrochemical impedance spectroscopy (EIS) were carried out in 6 M aqueous KOH electrolyte. The two electrodes were placed inside a split test cell (EQ-STC, MTI Corporation, USA) to design the ASC. The electrodes were separated by Whatman 42 filter paper impregnated with 6 M aqueous KOH. The loading mass of the (three electrode) electrode was 176, 223 and 280 μg for SAC@Ni, RGO@Ni and SAC-RGO@Ni, respectively.

3. Results and Discussion

3.1 Structural and Morphological Analysis

The FT-IR spectra of GO, RGO, SAC and SAC-RGO was carried out to investigate the reduction and functionalization of GO (Fig. 1). Pure GO shows peaks at 1731, 1396, 1234 and 1063 cm^{-1} due to the presence of carboxyl, deformation vibration of -C-OH, stretching vibration of epoxy and alkoxy groups, respectively.^{10,23-25} The restoration of C=C stretching and the removal of peaks related to the oxygen functional groups in the spectrum of RGO and SAC-RGO confirms the successful reduction of GO during the electro-deposition. The peaks at 1204 and 1042 cm^{-1} are ascribed to the stretching vibration peaks of -S=O of -SO₃H in SAC.^{10,24,25} These peaks are also present in the SAC-RGO confirming the functionalization of RGO by SAC. Further, the peaks related to the oxygen functional groups disappear in SAC-RGO and the appearance of C=C peak confirms the reduction as well as functionalization of the graphene. The intensity of the -S=O peaks are low in SAC-RGO as compared to SAC and a red shift (from 1042 to 1231 cm^{-1}) can be noticed in SAC-RGO due to the π - π interaction.^{10,24,25,26}

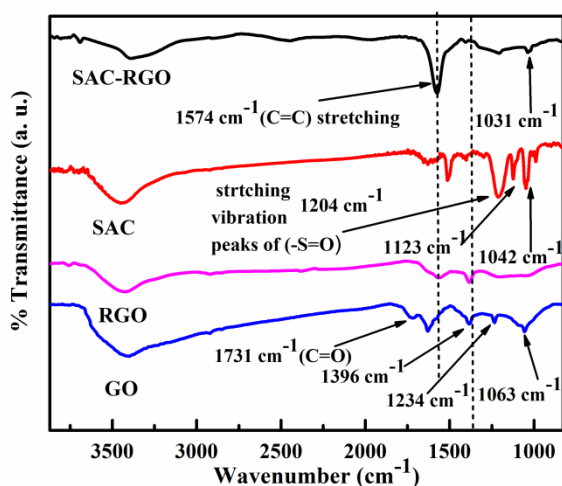


Fig. 1 FT-IR spectra of GO, RGO, SAC and SAC-RGO.

Fig. 2a shows the XRD pattern of GO and SAC-RGO. The (002) peak of graphite appears at 26.7° corresponding to the interlayer spacing of 0.34 nm.²³ This peak shifted to 10.2° for

GO. The increase in interlayer spacing is attributed to the presence of oxygen functional groups in the interlayer spacing of GO.²³ The appearance of (002) peak at 24.2° for SAC-RGO suggests the reduction or the removal of oxygen functional groups during electro-deposition.²³ Another small peak of SAC-RGO at 43.2° may be the result of carbon erosion related to redox reaction on the (100) crystal plane of graphite.³ Fig. 2b shows the Raman spectra of GO and SAC-RGO. Graphene prepared by chemical vapour deposition and pure graphite show two characteristic peaks: the G-band at 1575 cm^{-1} and the 2D band at $\sim 2700 \text{ cm}^{-1}$.^{23,27} The bond stretching of sp^2 carbons results in the appearance of G peak and the two phonon double resonance process in the band structure of graphene layers is the reason of 2D peak. An additional sharp peak (D-band) arises at $\sim 1355 \text{ cm}^{-1}$ mostly for the chemically derived graphene which is due to the presence of disorder or defects in the graphene moiety.²³ Change in the defect level can be observed by calculating the I_D/I_G ratio (I_D = intensity of D band, I_G = intensity of G band of Raman spectra) as it provides information about the variable ratios of $\text{Csp}^3/\text{Csp}^2$.^{10,28} In the present study, the starting material GO shows high I_D/I_G ratio (~ 1.06) due to the presence of oxygen functional groups which may interrupt the π - π^* bonds.^{10,24} The Raman spectra of SAC-RGO show very low I_D/I_G ratio (0.41) as well a sharp 2D peak. The functionalization of SAC-RGO was confirmed by the FT-IR spectra analysis. Thus, the low I_D/I_G ratio indicates the removal of oxygen functional groups and intact sp^2 network of graphene. The π - π interaction of SAC and the basal plane of graphene results in the functionalization of RGO without the formation of covalent bond or any defect. Furthermore, the sharp 2D peak indicates that the SAC can acts as the spacer element between the graphene layers preventing the restacking after reduction of GO. Fig. 2c presents the C1s XPS of SAC-RGO. The peaks at 284.4 and 285.2 eV are attributed to the presence of C-C/C=C and C-S bonds further confirming the functionalization of RGO.¹⁰ The peak at 288.8 eV corresponds to the C=O of carboxylic or/carbony groups of RGO.¹⁰ The oxidizing reaction normally takes place at positive electrode. However, the GO is reduced to RGO due to the deoxygenation process followed by the electrochemical reaction (similar to the Kolbe reaction). The surface of GO contains -COOH and -OH groups. It is proposed that the -OH groups is possibly oxidized to -COOH groups at the anode. The -COOH groups are eliminated by Kolbe type reaction as described by An et al.²⁹

$\text{Ar-COO}^- \rightarrow \text{Ar-COO}^\cdot + \text{e}^-$ (oxidation of carboxylate)
 $\text{ArCOO}^\cdot \rightarrow \text{Ar}^\cdot + \text{CO}_2$ ("oxidative decarboxylation")
 $2\text{Ar}^\cdot \rightarrow \text{Ar-Ar}$ (dimerization of radicals)

[Ar represents the aromatic backbone of GO or graphene].

The GO sheets are negatively charged, as the abundant deprotonated carboxylate groups are present and thus, move towards the anode. It is anticipated that no electrochemical reaction occurred before the electronic contact to the anode. After the deposition, GO loses electrons resulting the elimination of -COOH groups. The unpaired electrons formed

by the Kolbe-like loss of CO₂ are then free to migrate through the GO framework to form covalent bonds.

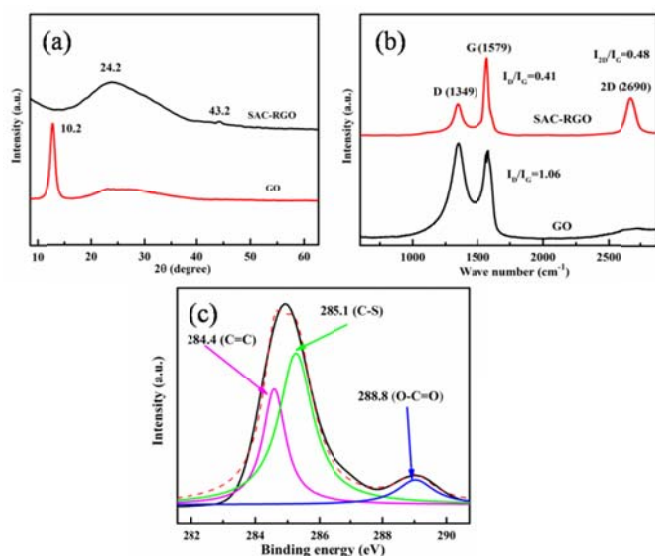


Fig. 2 (a) XRD of GO and SAC-RGO, (b) Raman spectra of GO and SAC-RGO and (c) XPS of SAC-RGO.

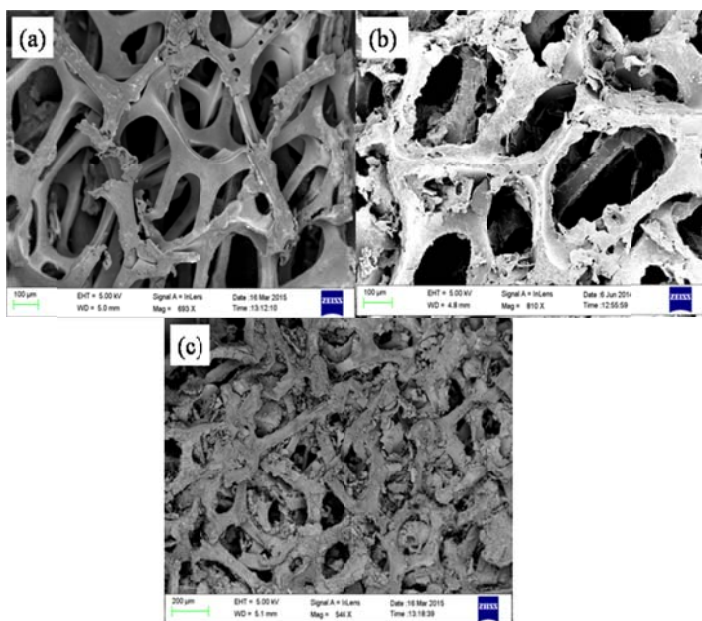


Fig. 3 FE-SEM images of (a) SAC@Ni, (b) RGO@Ni and (c) SAC-RGO@Ni.

The morphology, size, and structure of SAC@Ni, RGO@Ni and SAC-RGO@Ni were investigated by FE-SEM and TEM image analysis. Fig. 3(a-c) shows the FE-SEM image of SAC@Ni, RGO@Ni and SAC-RGO@Ni. SAC@Ni shows a lesser amount of material deposited on the nickel mesh. The background of three dimensional nickel foam of RGO@Ni is covered by the RGO sheets and the higher amount of deposition clearly be seen for SAC-RGO@Ni. GO has electronegative oxygen functional groups and the ionic conductivity of the electrolyte

increases in presence of SAC resulting simultaneous electro-deposition and functionalization of the deposited materials.

Fig. 4(a,b) represents the high resolution FE-SEM image of SAC-RGO@Ni. The inset of Fig. 4a shows the image of bare nickel foam. Fig. 4b shows the deposited SAC-RGO has sheets like structure. The formation of the folded graphene sheet is confirmed by the TEM image of SAC-RGO (Fig. 4c). The SAED pattern of SAC-RGO shows the poly crystalline nature due to the presence of SAC on the RGO sheets.¹⁰

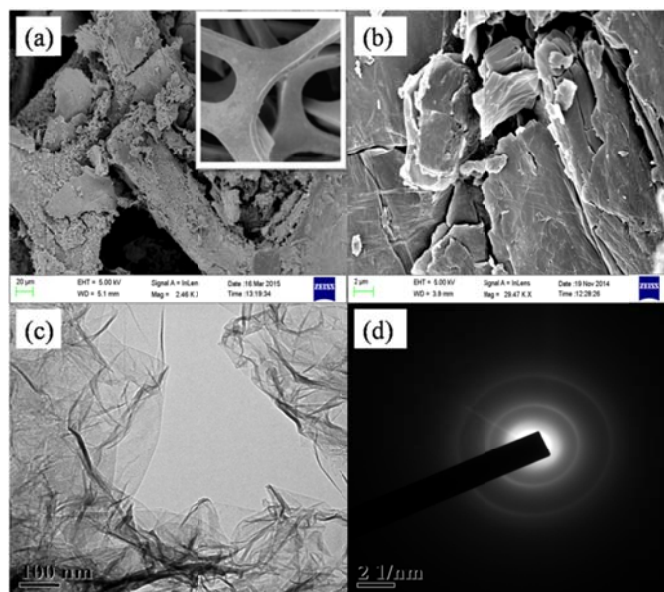


Fig. 4 (a) High resolution FE-SEM image of SAC-RGO@Ni. The inset view compares the bare nickel foam. (b) High resolution FE-SEM image of single mesh of the deposited nickel foam, (c) TEM image and (d) SAED pattern of SAC-RGO.

The electrical conductivity can be measured by the formula:

$$\sigma = \frac{1}{\rho} = \frac{1}{4.532 \times R \times d}$$

, where ρ is the resistivity of the material. R and d are the resistance and thickness of the prepared pellet.^{10,12} The high and low current ranges during the measurement were recorded in the range of 20×10^{-6} to -20×10^{-6} A, and the delta voltage step was fixed at 100 mV s^{-1} for all the samples. The electrical conductivity of GO, SAC, RGO and SAC-RGO was found to be 0.003, 0.31, 701 and 784 S m^{-1} , respectively. The high electrical conductivity of SAC-RGO may be due to the good reduction as supported by the FT-IR and Raman spectra analysis.

3.2 Electrochemical performance analysis

Electrochemical impedance spectroscopy gives a clear view about the interaction of the electrode materials with the electrolyte. Fig. 5 shows the Nyquist plot of SAC@Ni, RGO@Ni and SAC-RGO@Ni. The intersection of the high frequency

region to the real axis of the Nyquist plot is the solution resistance.¹² It arises due to the non faradaic charge transfer between the electrode and electrolyte and directly depends on the electrical conductivity of the electrode materials. Fig. S1 of supporting information represents the Zview fitting of EIS, equivalent circuits and corresponding results of (a) SAC@Ni, (b) RGO@Ni and (c) SAC-RGO@Ni. The Zview fitting provides the accurate measurement of the solution resistance, faradic resistance, Warburg resistance and diffusion time constant (Table 1). Electrically conducting RGO@Ni and SAC-RGO@Ni show very low solution resistance of 0.51 and 0.6 ohm, respectively.³⁰ The non-conducting SAC@Ni has high solution resistance of ~8.92 ohm. The faradic charge transfer resistance of SAC@Ni is also very large (~5.36 ohm) as compared to the RGO@Ni and SAC-RGO@Ni (0.21 and 0.51 ohm, respectively). Thus, the presence of graphene enhances the redox activity for RGO@Ni electrode. The diffusion time constant (W-T) is directly related with the diffusion path of electrolyte.^{10,31} The comparatively large W-T of RGO@Ni may due to the restacking of graphene layer after reduction.

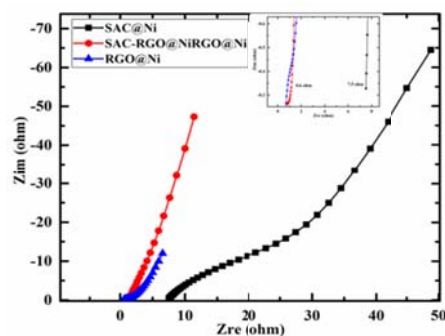


Fig. 5 EIS of SAC@Ni, RGO@Ni and SAC-RGO@Ni.

Table 1 Comparison of Zview fitting of nyquist plot of SAC@Ni, RGO@Ni and SAC-RGO@Ni.

	SAC@Ni	RGO@Ni	SAC-RGO@Ni
Rs	8.92	0.51	0.6
Rp	5.36	0.21	0.51
W-R	48	2.45	2.12
W-T	0.12	0.28	0.02

The CV of SAC@Ni, RGO@Ni and SAC-RGO@Ni was carried out at a scan rate of 10 mV s⁻¹ and is shown in Fig. 6. SAC@Ni shows the potential window in the positive region of 0-0.7 V with a prominent pseudo peaks. The appearance of redox peak in the CV curve of SAC@Ni may be attributed to the presence of -SO₃H functionalities.¹⁰ The redox mechanism of the SO₃H functionalities can be explain by the following reversible reaction

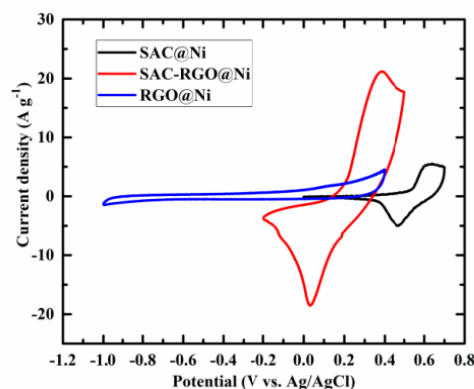
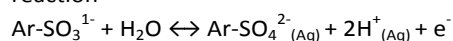


Fig. 6 CV plot of SAC@Ni, RGO@Ni and SAC-RGO@Ni at a scan rate of 10 mV s⁻¹.

The oxidation and reduction peaks of SAC@Ni are visible at 0.6 and 0.45 V, respectively. RGO@Ni behaves like a negative electrode materials. SAC-RGO@Ni shows the potential window of -0.2 to 0.5 V with oxidation and reduction peak at 0.38 and 0.04 V, respectively. The positive shift of redox peaks in SAC@Ni as compared to the SAC-RGO@Ni may be attributed to the decrease in pH of the aqueous electrolyte. The π - π interaction between SAC and RGO prevents the desolation of SAC in the aqueous electrolyte. However, SAC was physically adsorbed on the Ni-foam in SAC@Ni electrode. Therefore, the SAC started to solubilise as soon the electrode was dipped in the aqueous electrolyte resulting the decrease in electrolyte pH. Interestingly, it is found that the transparent aqueous KOH electrolyte changed to reddish while dipping SAC@Ni electrode. In contrast, the colour of the electrolyte remains unchanged for SAC-RGO@Ni electrode. Therefore, the shift of redox peaks in the SAC-RGO@Ni electrode is possibly attributed to the change in electrolyte pH as reported earlier.³²⁻³⁴ The specific capacitance can be calculated according to

the equation: $C_{cv} = \left(\int IdV \right) / mv$, where C_{cv} is the specific capacitance (F g⁻¹), I is the response current density (A g⁻²), V is the potential window, v is the scan rate (mV s⁻¹), and m is the deposited mass on the electrode.^{3,6} SAC@Ni, RGO@Ni and SAC-RGO@Ni have the specific capacitance of 195, 225 and 1090 F g⁻¹, respectively. The poor specific capacitance of SAC@Ni can be due to its electrically non conducting property and large solution resistance. However, the low specific capacitance of RGO@Ni may be due to the restacking of RGO layers after reduction and deposition on the nickel foam. During the layer by layer electro-deposition, the SAC acts like the spacer element in between the individual RGO sheets. The -SO₃H functionalities of SAC increases the electrode/electrolyte interaction due to its hydrophilic nature and the superior pseudo activity can be achieved for SAC-RGO@Ni. Furthermore, synergistic effect of both EDLC and pseudo reaction in SAC-RGO@Ni electrode provides very high

specific capacitance of $\sim 1090 \text{ F g}^{-1}$. The main advantage of the electrodeposited electrode is to avoid the use of any polymer additive and the electrical conductivity of the modified electrode remains un-affected. At the same time, proper distribution of the active material to the current collector surface is possible.

Fig. 7a represents the CV plot of SAC-RGO@Ni at different scan rate. Current response increases accordingly with increasing the scan rate and the pseudo peaks remain almost at the same position. The CV curves of SAC@Ni and RGO@Ni studied at different scan rate are represented in Fig. S2 of supporting information. The variation of specific capacitance with scan rate of SAC@Ni, RGO@Ni and SAC-RGO@Ni is shown in Fig. 7b. The specific capacitance of SAC@Ni, RGO@Ni and SAC-RGO@Ni are 83, 208 and 767 F g^{-1} , respectively at a scan rate of 200 mV s^{-1} . The transport of electrons through the external circuit's increases significantly as compared to the diffusion of ions within the electrodes and electrolytes at higher scan rates resulting the deterioration of specific capacitance. The CV of bare nickel foam was carried out in order to study the contribution of the current collector to the performance of electrode materials (Fig. S3 of the supporting information). The nickel foam is used as the current collector because the electrical conductivity of nickel foam is very high but the charge storage capacity is very low and as a result the specific capacitance is very small. The CV plot of nickel foam shows very low current response and the specific capacitance is also very low ($\sim 0.52 \text{ F g}^{-1}$). The retention in specific capacitance at a scan rate of 200 mV s^{-1} is only 41% for SAC@Ni. The rate capability increases for the graphene congaing samples (Fig. S4 of supporting information). Improved capacitance retention (65 and 70%) can be observed for RGO@Ni and SAC-RGO@Ni electrodes.

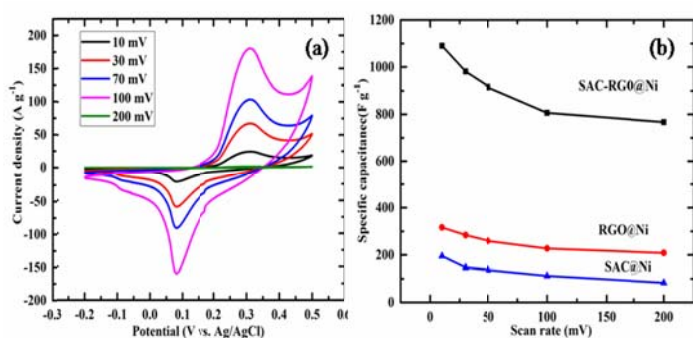


Fig. 7 (a) CV of SAC-RGO@Ni at different scan rates, and (b) variation of specific capacitance with scan rate of SAC@Ni, RGO@Ni and SAC-RGO@Ni.

The three electrode CD profiles of SAC-RGO@Ni are shown in Fig. 8a. It shows prolong discharging time up to 0.2 V after a large IR drop (up to 0.3 V). Most of the capacitive performance lies in 0.2 to 0.3 V regions and this potential difference can be

termed as an effective zone of the discharging profile. Fig. 8b shows the decreases in specific capacitance with increasing current density. The specific capacitance can be calculated

$$C_{\text{CD}} = \frac{I \times \Delta t}{\Delta V \times m}$$

from the CD following the relation: C_{CD} is the specific capacitance (F g^{-1}), I is the discharging current (A g^{-2}), ΔV is the potential window (V) and m is the deposited mass on the electrode.^{6,7,35} The maximum specific capacitance is $\sim 1067 \text{ F g}^{-1}$ at a current density of 3.5 A g^{-1} . The electrode shows $\sim 68 \%$ retention in specific capacitance at very high current density of 6 A g^{-1} . Fig. S5 of the supporting information shows SAC-RGO@Ni cannot be fully charged at a low current density of 1 A g^{-1} . The large IR drop may be the reason behind it. The SAC-RGO@Ni suffers from low coulombic efficiency (78%) but shows very high specific capacitance of 1235 F g^{-1} at a current density of 2 A g^{-1} .

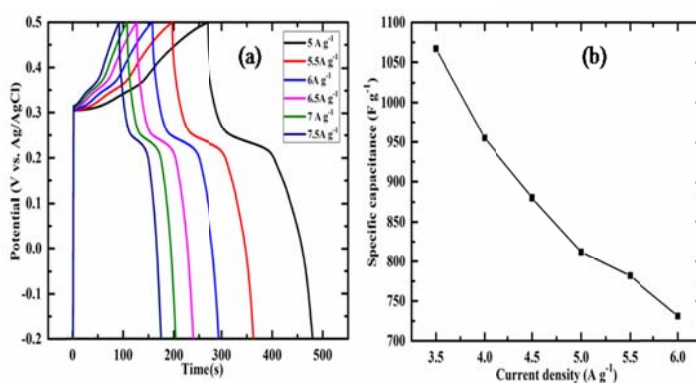


Fig. 8 CD of SAC-RGO@Ni at different current density and (b) variation of specific capacitance with current density SAC-RGO@Ni

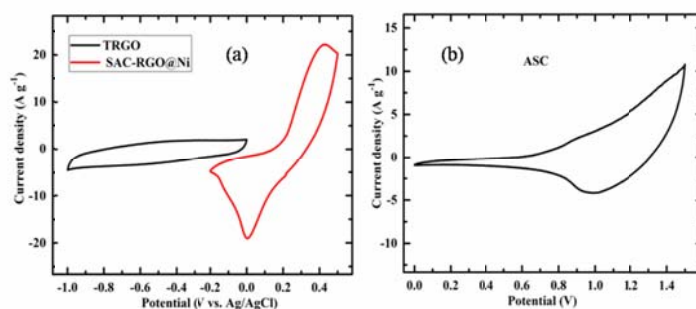


Fig. 9 (a) Comparison of CV of positive and negative electrode materials, and (b) CV of ASC.

The ASC device was designed in order to increase the working potential. The TRGO was selected as the negative electrode. The CV of SAC-RGO and TRGO (Fig. 9a,b) shows that the ASC can be operated with a working potential of 1.5 V. The ratio of deposited mass on the electrodes was calculated according to

the charge balance relation: $\frac{m_+}{m_-} = \frac{C_- \times \Delta E_-}{C_+ \times \Delta E_+}$, where m_+ and m_- are the mass of the positive and negative electrodes, C_+ and ΔE_+ are the specific capacitance and working potential (calculated from the three electrode CV) for positive electrode, C_- and ΔE_- are the specific capacitance and working potential of the negative electrode measured at the same scan rate.^{3,6,36,37,38,39}

Fig. 10(a,b) represents the CV and CD of ASC. It shows high specific capacitance of $\sim 353 \text{ F g}^{-1}$ at 10 mV s^{-1} scan rate. The current response increases with increasing the scan rate and the CV nature remains undistorted at high scan rate of 200 mV s^{-1} . The positive electrode material was suffered from large IR drop during three electrode measurement, but the improvement can be noticed as there is almost zero IR drop in ASC. The CD plot shows the ability of the ASC cell to work with the high current density. Fig. 11a shows the variation of specific capacitance of ASC with increasing current density. The calculated specific capacitance was 280 F g^{-1} at a current density of 10 A g^{-1} . The specific capacitance decreases with increasing current density due to the deterioration of ionic diffusion and adsorption at the electrode/electrolyte interface.^{10,40,41} The CD of ASC was studied up to 22 A g^{-1} current density and the specific capacitance was found to be 165.7 F g^{-1} . Most of the capacitive performance exhibited by the ASC lies in the potential window of 1.5 to 0.75 V followed by a sharp fall during discharging. As a result, the ASC can maintain at least 0.75 V during 93% of total discharging profile and only 7% discharging time is wasted. The effective specific capacitance can be calculated during discharging in the potential window of 1.5 to 0.75 V . The effective specific capacitance of ASC was measured to be 495 F g^{-1} at 10 A g^{-1} .

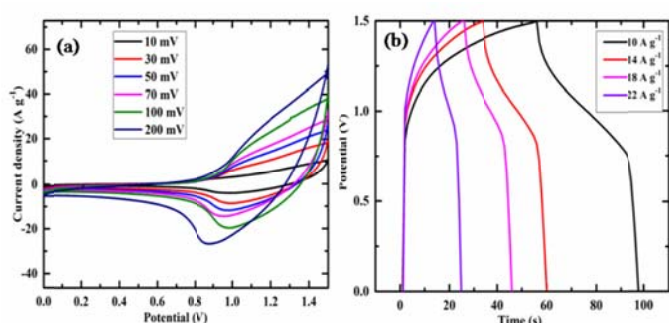


Fig. 10 (a) CV of ASC at different scan rates, and (b) CD of ASC different current density.

The energy density (ED) and power density (PD) can be

$$E = \int_{t1}^{t2} \frac{I}{m} V dt$$

calculated according to the formula: and

$$P_D = \frac{E_D}{\Delta T}, \text{ where } I \text{ is the discharging current, } m \text{ is the mass}$$

(The loading mass of asymmetric cell is $740 \mu\text{g}$), V is the potential window and dt is the discharging time. The limit of the integration are t_2 (end of discharging) and t_1 (start of discharging).^{3,6,7,42,43} Fig. 11b represents the Ragone plot of ASC. The present ASC can deliver a high energy density of 88.9 W h Kg^{-1} at a power density of 7500 W Kg^{-1} . Even at a very high power density of $16,500 \text{ W Kg}^{-1}$, the ASC can able to reach an energy density of 51.7 W h Kg^{-1} . The variation of effective specific capacitance and energy density with increasing current density has been described in Fig. S6 of the supporting information. Considering the effective potential window from 0.75 to 1.5 V a large effective energy density of 116 W h kg^{-1} was achieved at a current density of 10 A g^{-1} .

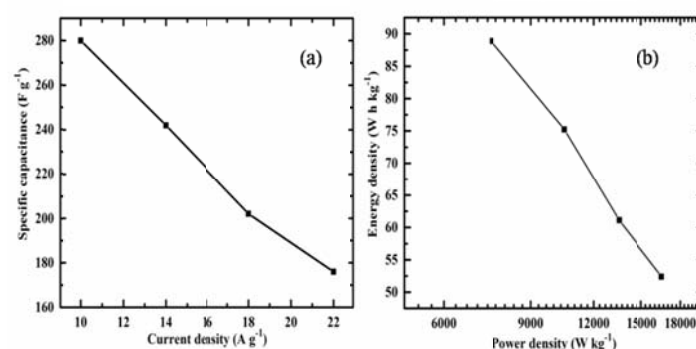


Fig. 11 (a) Variation of specific capacitance with current density, and Ragone plot of ASC.

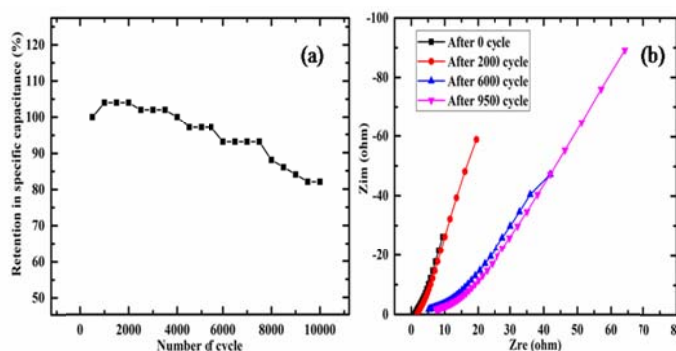


Fig. 12 (a) Charge-discharge cyclic stability test and (b) EIS after different charge-discharge cycles of ASC.

The stability of the ASC cell was tested up to 10,000 charge-discharge cycles as shown in Fig. 12a. About 4% increase in capacitance value was noticed after 1st 500 cycles. Proper wetting of the electrolyte as well as improved electrode/electrolyte contact may be the reason behind it.^{40,43,44} The EIS of the ASC cell was taken in between cycles when the decrease in capacitance is observed (Fig. 12b). The Nyquist plots show that the specific capacitance decreases during the stability test due to the increase in solution resistance. It may be attributed to the loss of adhesion of the electrolyte in the electrode surface.^{10,45} The lower frequency

region of the Nyquist plot is a straight line inclined to the imaginary axis indicating conductive nature of the electrode materials.¹² The slope of the straight line decreases with increasing CD cycles and it suggests the degradation of diffusion path within the electrode materials.^{12,46} The presence of SAC-RGO on the nickel foam is clearly visible after 10,000 cycles as shown in Fig. S7 (a) of supporting information. The stable and unfractured morphology of nickel foam can be seen from the single nickel mesh of SAC-RGO@Ni (Fig. S7 (b)). Finally, ~88% retention in specific capacitance is observed after 10,000 charge-discharge cycles which is promising for the energy storage applications.

Conclusions

The SAC modified RGO was successfully deposited on the nickel foam through simple electro-deposition technique. The simultaneous electro-deposition, reduction and functionalization of GO was carried out in a single and cost effective method. The attachment of the -SO₃H groups on to the RGO moiety was confirmed by the FT-IR spectra and XPS analysis. The appearance of sharp 2D peak and very low I_D/I_G ratio in Raman spectra supports the reduction of the graphene oxide without hampering its conjugated sp² network. The presence of -SO₃H groups in SAC prevented the restacking of the graphene sheets allowing good penetration of the electrolyte for rich electrochemical activity. Highly electrical conductive SAC-RGO@Ni showed synergistic effect of both EDLC and rich pseudo activity with a specific capacitance of 1090 F g⁻¹. Large potential window of 1.5 V was achieved by designing the ASC cell with TRGO as the negative electrode. The ASC showed an effective discharging profile where ~93% of its total discharging occurred in the potential range of 1.5-0.75 V and generated very high effective specific capacitance of 495 F g⁻¹ at ~10 A g⁻¹. The ASC showed good rate capability and can retain 88% of its energy storage ability even after 10,000 cycles. Furthermore, very high energy and power density of 88.9 W h Kg⁻¹ and 16,500 W Kg⁻¹ of ASC suggest its convenience future for new generation high power consumable energy storage application.

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