**Reduced graphene oxide based ternary nanocomposite cathodes for high-performance aqueous asymmetric supercapacitors**

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**ABSTRACT**

Ternary nanocomposites have attracted increasing attention as efficient supercapacitor electrode materials. Here we report, the synthesis of a ternary hybrid nanocomposite by the introduction of crystalline RuO2 nanoparticles loaded carbon nanocoils (CNCs) as spacers in reduced graphene oxide (RGO). The RGO-(RuO2/CNCs) composite electrode exhibits a high specific capacitance of 725 F g-1 at a scan rate of 20 mV s-1 in three-electrode configuration. When used in symmetric two electrode configuration, it shows a specific capacitance of 436 F g-1 at a constant current density of 1 A g-1, which is nearly three times higher than that of pure RGO based electrode. An aqueous asymmetric supercapacitor fabricated using RGO-(RuO2/CNCs) as the positive electrode and RGO as the negative electrode is operational in an electrochemically stable potential window of 2V. The asymmetric capacitor exhibits a high energy density of 45 Wh Kg-1 at a power density of 1 kW kg-1 and retains an energy density of 41 Wh Kg-1 even at a high power density of 40 kW kg-1.

**KEYWORDS**: Ternary hybrid nanocomposite, RGO-(RuO2/CNCs), specific capacitance, energy density, cycle life

1. **Introduction**

From portable electronics and transportation systems to backup systems that complement renewable sources such as solar and wind, the demand for energy storage is expected to grow substantially well into the foreseeable future [[1](#_ENREF_1), [2](#_ENREF_2)]. Supercapacitors can act as a promising energy- storage alternative for rapidly growing electronic industry [[3](#_ENREF_3), [4](#_ENREF_4)]. But their lower energy density as compared to batteries is still a significant problem, which needs to be addressed for making these devices useful for everyday applications [[3](#_ENREF_3), [5](#_ENREF_5)]. The energy density of supercapacitors can be expressed as E = ½ CV2, where C is the device capacitance and V is the potential window of operation. This expression indicates that the energy density of supercapacitors can be improved either by improving the device capacitance using an electrode material with high surface area, excellent electrical conductivity, and high specific capacitance or by widening the electrochemically stable potential window [[3](#_ENREF_3), [6](#_ENREF_6)]. The asymmetric configuration of electrodes in aqueous electrolytes or the use of organic/ionic liquid electrolytes help in extending the potential window of operation [[7](#_ENREF_7)].

Reduced Graphene Oxide (RGO), due to its high electroactive surface area, good chemical stability, large in-plane conductivity, and excellent flexibility, has attracted significant research attention as the electroactive material for supercapacitor electrodes [[8-10](#_ENREF_8)]. However, these electrodes exhibit a low specific capacitance value (< 200 F g-1), as the graphene layers tend to agglomerate during the electrode preparation due to the π-π stacking and strong van der Waals interactions between individual layers, leading to a reduction in electrochemically active surface area [[9](#_ENREF_9), [11](#_ENREF_11)]. The restacking of graphene layers can be considerably reduced by the introduction of spacers between the layers. Both nanocarbon materials showing electric double layer capacitive (EDLC) behavior and pseudocapacitive materials (transition metal oxides or conducting polymers) showing faradaic behavior can act as efficient spacers for this purpose [[12-18](#_ENREF_12)]. The spacers ensure high electrochemical utilization of graphene layers and also contribute to the total capacitance of the system [[19](#_ENREF_19)].

Among the different pseudocapacitive materials, ruthenium oxide (RuO2), with its high theoretical specific capacitance (up to 2200 F g-1), proton-electron mixed conductive nature, wide potential window, ability to store charges reversibly, long cycle life, and high rate capability, is considered as the most promising candidate for supercapacitor applications [[12](#_ENREF_12), [20](#_ENREF_20), [21](#_ENREF_21)]. But high cost limits its practical applications, which can greatly be overcome by loading this material on a porous and conductive nanocarbon support. Reports suggest that when a pseudocapacitive nanomaterial is used in combination with a nanocarbon, synergistic effects of the combination enhances the electrochemical performance of the functional nanomaterials. If such a nanohybrid is introduced as the spacer between the graphene layers, the resultant ternary nanocomposite obtained can serve as a promising supercapacitor electrode material with excellent conductivity and high electroactive surface area[[12](#_ENREF_12), [20](#_ENREF_20)]. Carbon nanofibers with helical morphologies, widely known as carbon nanocoils (CNCs) possess excellent electrical conductivity, high porosity, and oxidation resistance nature [[22-26](#_ENREF_22)]. These qualities make them an ideal carbon support for the dispersion of pseudocapacitive nanomaterials [[23](#_ENREF_23), [26](#_ENREF_26)].

The thermodynamically stable potential window of the electrolyte decides the operating voltage of the supercapacitor. Because the thermodynamic window of water is 1.23 V, water-based electrolytes work with a relatively small equivalent series resistance (ESR) in a maximum potential window of 1 V [[27](#_ENREF_27)]. By contrast, the operational voltage varies from 3 to 5 V for the organic electrolyte. But the high equivalent series resistance (ESR) value prevents from attaining high power density value for organic electrolyte based supercapacitors [[28](#_ENREF_28)]. Moreover, low conductivity, high cost, toxic nature, and the tendency to become unstable in the presence of activated carbon based electrodes make them less attractive for practical applications. The operational potential window of aqueous supercapacitors can be widened by designing asymmetric configurations. Aqueous electrolytes are having the added advantages of low cost, high ionic conductivity, environmentally safe nature, stability in the air, and non-inflammability [[29](#_ENREF_29)].

Herein, we aim to study the spacer effect of RuO2/CNCs in RGO for maximizing the capacitance of the latter. The introduction of spacers significantly improves the electroactive surface area of the RGO-(RuO2/CNCs) composite, without a detrimental loss of electrical conductivity. The composite electrode exhibited a specific capacitance of 725 F g-1 at a scan rate of 20 mV s-1. Systematic comparison of the performances of symmetric supercapacitor based on RGO-(RuO2/CNCs) composite electrodes and an asymmetric supercapacitor comprised of a RGO-(RuO2/CNCs) composite cathode and an RGO anode (with a cell voltage of 2 V) demonstrates the obvious enhancements in both energy and power densities in the asymmetric design.

1. **Experimental**

***2.1 Synthesis of RGO-(RuO2/CNCs) ternary nanocomposites***

The RGO-(RuO2/CNCs) composite was synthesized by the ultrasonication of RGO and RuO2/CNCs. RGO was prepared by the hydrothermal reduction of graphite oxide (GO) synthesized using modified Hummer’s method. 37.5 mL of 0.5 mg mL-1 GO aqueous solution (basic, pH~10) prepared by probe ultrasonication (160 W) for 1 h was sealed in a 50 mL teflon-lined autoclave and maintained at 180 for 6 h. It was then cooled to room temperature; the resultant black product was filtered and washed using DI water. For the synthesis of RuO2/CNCs, 1 g of RuCl3. 3H2O was added to a uniform dispersion of CNCs in water (200 mg in 500 mL, pH~7). The mixture was refluxed at 120 ºC for 6 h. After the reaction, the precipitate was separated, dried, and calcined at 300 ºC, leading the formation of RuO2/CNCs. RGO and RuO2/CNCs composites in the ratio 8:2 by weight were dispersed in 200 mL of distilled water by ultrasonication for 5 h to obtain a homogeneous RGO-(RuO2/CNCs) suspension. Finally, the solid was filtered, and washed several times with distilled water and alcohol, dried at 80 ˚C for 5 h in a vacuum oven.

***2.2 General characterization of composites***

The nanocomposites were characterized by a powder X-ray diffraction system (XRD, PAN analytical X’pert Pro) equipped with Cu Kα radiation (λ= 0.15406 nm) and the composition of RuO2/CNCs was analyzed using thermogravimetric analysis (EXSTAR TG/DTA 6200). BET surface areas of the materials were measured using surface area and porosimetry system ‘Micromeritics’ (Micromeritics ASAP 2020) at 77 K. The surface morphology and microstructure of the nanomaterials were investigated using scanning electron microscopy (SEM, JEOL JSM-5600 LV) and transition electron microscopy (TEM, FEI, Tecnai G2 30LaB6, ST with EDAX) analyses. The elemental presence was identified using energy dispersive X-ray analysis (EDAX).

***2.3 Preparation of electrodes and electrochemical measurement***

Symmetric capacitors were fabricated using the nanocomposites. Supercapacitor electrodes of 1 cm2 area were prepared using RGO and RGO-(RuO2/CNCs) by the following procedure. The active material was mixed with polytetrafluoroethylene (PTFE) binder in a mass ratio of 95:5 and dispersed in ethanol by ultrasonication. The resulting mixture was coated onto the conductive carbon cloth (ELAT, Nuvant Systems Inc.) substrate, which was followed by drying at 100 ˚C for 12 h in a vacuum oven. Two symmetric electrodes, separated by a thin polymer separator (Celgard® 3501) in 30 wt % KOH aqueous electrolyte, were sandwiched in a standard electrochemical cell (ECC-std, EL-Cell GmbH). Each electrode contained ~**4 mg** of active material, and this mass was used in the calculation of specific capacitance of the symmetric supercapacitors.

Specific capacitance values of RGO and RGO-(RuO2/CNCs) electrodes were also measured in three electrode configuration. This measurement was conducted in 30 wt % KOH aqueous electrolyte, with a platinum foil and an Ag/AgCl respectively as the counter and the reference electrodes and the (RGO-(RuO2/CNCs) or RGO) based electrode as the working electrode. The RGO-(RuO2/CNCs)//RGO asymmetric supercapacitor is constructed using RGO (mass = 5.6 mg) as the negative electrode material and RGO-(RuO2/CNCs) (mass = 2 mg) as the positive electrode material, Celgard® 3501 membrane as the polymer separator, and 30 wt% KOH as the aqueous electrolyte medium. The loading mass ratio of active materials in the electrodes was estimated by the charge balancing principle, details of which are explained in section 3.

The electrochemical properties of the supercapacitor electrodes were studied by cyclic voltammetry (CV), galvanostatic charge/discharge (CD) and electrochemical impedance spectroscopy (EIS) measurements. All these measurements were carried out at room temperature using a VMP3 Biologic electrochemical workstation. EIS measurements were conducted at a dc bias of 0 V in the frequency range from 100 kHz to 1 mHz with a sinusoidal signal of 10 mV. EIS data was analyzed using complex plane impedance plots (Nyquist plots).

Specific capacitance (*Csp*) of symmetric supercapacitors were calculated from the cyclic voltammogramms and charge-discharge curves according Eq. (1) and (2)

 (1)

where ‘*i*’ is average cathodic current of CV loop and ‘*s’* is the scan rate.

 (2)

where ‘*I*’ is the constant current for charge- discharge,  is slope of the discharge curve.

Specific capacitance for electrodes in three electrode configuration is calculated as

 (3)

The cell capacitance (C) and the gravimetric capacitance based on the total mass of active materials in both the electrodes (Cg) are calculated from the slope of the discharge curve, as per the following equations

 and  (4)

Where ‘*I*’ is the constant current for charge- discharge and  is the slope of the discharge curve. ‘*M*’ is the total mass of active materials in both electrodes.

1. **Results and Discussion**

RGO-(RuO2/CNCs) are prepared by ultrasonic mixing of RuO2/CNCs (20 wt %) and RGO (80 wt %) as illustrated in Fig.1. It is expected that the RuO2/CNCs nanohybrids will act as excellent spacers between individual RGO layers and will increase the surface area of the resultant composite. Powder X-Ray Diffraction patterns of the components and the ternary hybrid nanocomposite are shown in Fig. 2a. The peaks in the XRD patterns of CNCs and RGO are indexed to the reflections of hexagonal graphite (JCPDS card No. 75-1621). The shift in the 2θ value of the (002) peak can be attributed to the structural difference of CNCs and RGO. The peaks marked with an asterisk, present in the XRD pattern of RuO2/CNCs, in addition to the graphitic peaks, correspond to characteristic diffraction peaks of the tetragonal RuO2 nanoparticles (JCPDS card No. 40-1290). The (002) Peak from graphitic carbon overlaps with the (110) peak from RuO2. The absence of any other crystal phase attributable to another covalent state of Ru indicates the high purity of RuO2 phase in RuO2/CNCs. XRD pattern of the ternary hybrid nanocomposite also shows the presence of carbon and RuO2. The amount of RuO2 present in RuO2/CNCs binary nanocomposite is determined by thermogravimetric analysis (TGA). TGA curves of CNCs and RuO2 dispersed CNCs are shown in Fig. 2b. Weight loss between 400 ◦C and 750 ◦C in the TGA curves can be attributed to the burning of CNCs. The pure CNC sample is having a purity of 90%. TGA curve for RuO2/CNCs shows a weight loss of 25% over the above-mentioned temperature range, indicating that RuO2/CNCs binary composite contains 75% of RuO2 and 25% of CNCs. The amount of sample used for each TGA analysis is nearly 10 mg. TGA measurements were repeated several times to confirm the chemical composition of RuO2/CNCs nanocomposite, and the result shown in Figure 2 (b) is a representative data.

The Brunauer–Emmett–Teller (BET) surface area values of the CNCs, RuO2/CNCs, RGO and RGO-(RuO2/CNCs) are calculated from their nitrogen adsorption and desorption isotherms

(Fig. 2c) as 98.4, 353.7, 347.2 and 600.6 m2 g-1 respectively. Isotherms exhibit distinct loops in the range of 0.45 –1.0 P/P0, suggesting the mesoporous nature of these samples. BET surface area value of the ternary hybrid composite is nearly two times as compared to pure RGO sample, indicating that RuO2/CNCs acts as an efficient spacer between graphene layers. Hence, the RGO-(RuO2/CNCs) can offer more electrolyte accessibility, when used as an electrode material in supercapacitors. Fig. 2d shows the pore size distributions of the samples calculated from adsorption isotherms using Barret-Joyner-Halenda (BJH) method. BJH adsorption cumulative volume of pores between 1.70 nm and 300.00 nm diameter for CNCs, RuO2/CNCs, RGO and RGO-(RuO2/CNCs) are 0.24418, 0.34312, 0.53206, and 1.30911 cm3/g respectively.

Fig. 3(a), (b), (c) and (d) respectively shows the scanning electron microscopy (SEM) images of CNCs, RuO2/CNCs, RGO, and RGO-(RuO2/CNCs). SEM image of CNCs (Fig. 3(a)) indicates that these are single helical coils with twisted forms similar to a-helix proteins. The introduction of RuO2 nanoparticles does not damage the morphology of CNCs, except making the surface a bit rougher by the direct growth of RuO2 particles (Fig. 3 (b)). The wrinkled or curved morphology of the RGO nanosheets is evident from the SEM image shown in Fig. 3(c). SEM image of the ternary composites shows the presence of both RGO and RuO2/CNCs. The curved morphology of the nanosheets considerably prevents the RGO from restacking and contributes to the mesoporous nature as evident from the inset of Fig. 3(d). **Figure S1 (b)** shows the energy dispersive analysis of X-rays (EDAX) pattern of RGO- (RuO2/CNCs) composite for the area shown in SEM image **Fig. S1 (a)**. EDAX analysis gives the local concentration of different elements present in the ternary hybrid composite. EDAX pattern indicates that the nanocomposite contains the elements ruthenium, carbon, and oxygen. **Fig. S1(a)** shows the presence of RuO2/ CNCs spacers in the RGO matrix.

Transmission electron microscopy (TEM) analysis can be used as a powerful tool to obtain more detailed microstructure information of the nanocomposites. TEM image of the RGO (Fig. 4(a)) clearly indicates the wrinkled nature of graphene nanosheets. Low and high-resolution TEM images of functionalized CNCs shown in **Fig. S2 (a) and (b)** respectively reveals that CNCs are coiled carbon nanofibers and are having an average diameter in the range of 70-100 nm. Fig. 4(b) and 4(c) respectively show the low and high-resolution TEM images of RuO2/ CNCs. Samples used for the TEM measurements were prepared by the dispersion of RuO2/CNCs in ethanol by ultrasonication, leading to the breakdown of the CNCs. And the quantity of the sample used for such measurements is negligibly small. The density of CNCs is much lower than that of the RuO2 nanoparticles. Moreover, the particle size of RuO2 is less than 2 nm, and it makes a uniform coating on the surface of CNCs. TEM images clearly indicate the presence of tiny nanoparticles throughout the surface of CNCs (**Fig. S3 (a-c)).** The presence of ruthenium, carbon and oxygen is further confirmed from the EADX pattern of RuO2/CNCs shown in **Fig. S3 (d).** EDAX measurements give only local concentration the various elements present in the RuO2/CNCs. Whereas, TGA is a reliable and well-known technique used for the determination the chemical composition of metal oxide/nanocarbon composites.

These micrographs indicate a uniform distribution of nanocrystalline RuO2 particles with a mean particle size less than 2 nm, throughout the surface of CNCs. The Selected area electron diffraction (SAED) pattern corresponding to the area shown in Fig. 4(c) is given as the inset of Fig. 4(c). The SAED pattern indicates the polycrystalline nature of RuO2 nanoparticles. The diffraction rings in the pattern can be indexed to reflections from tetragonal RuO2 nanoparticles, and the results agree well with the PXRD results. Dispersion RuO2 on the surface of CNCs could significantly reduce the quantity of RuO2 required in the electrode layer, appropriate for the practical utilization of valuable ruthenium metal. Curved nature of the graphene nanosheets are further confirmed from the TEM image of the RGO- (RuO2/CNCs) composite (Fig. 4 (d)), showing the presence of both RGO and the hybrid spacer RuO2/CNCs.

Aqueous symmetric supercapacitors based on the RGO-(RuO2/CNCs) nanocomposite electrodes were fabricated, and their electrochemical performances were compared to that of symmetric capacitors based on pure RGO, pure CNCs, and RuO2/ CNCs. Cyclic Voltammograms (CV) for symmetric supercapacitors based on RGO and RGO-(RuO2/CNCs) samples, measured in a potential window of 0 to 1 V at different scan rates of 5,10, 20, 50 and 100 mV/s, are shown in Fig. 5 (a) and (c) respectively. Both the devices exhibit nearly rectangular CV loops, which are characteristics for supercapacitors with excellent capacitance behavior. Galvanostatic charge-discharge (CD) curves for RGO and RGO-(RuO2/CNCs) based symmetric supercapacitors at different constant current densities are shown in Fig. 5(b) and (d) respectively. The shapes of CD curves of both the supercapacitors are nearly triangular, with reduced internal resistance at the beginning of the discharge curve. Duration of the charge-discharge process for the RGO-(RuO2/CNCs) based capacitor is greater than that of RGO based one. The porous and conductive nature of the electrode materials facilitating fast electrolyte diffusion may be responsible for the lowering of internal resistance of the supercapacitors.

Fig. 6 (a) shows the comparison of CV loops of aqueous symmetric supercapacitors based on CNCs, RGO, RGO/CNCs, RuO2/CNCs, and RGO-(RuO2/ CNCs) electrodes with the same mass loading at a scan rate of 10 mV s-1. In each case, the CV curves exhibit a different area indicating a different level of stored charge. CV curves for all the capacitors retain a nearly rectangular shape, characteristic of that of an ideal EDLC capacitor. From the CV loops specific capacitances of 121, 159, 224, 309, and 434 Fg-1 respectively are calculated for the symmetric capacitors based on CNCs, RGO, RGO/CNCs, RuO2/CNCs, and RGO-(RuO2/ CNCs) electrodes. From Fig. 6(a), it is also evident that the capacitive contribution from the carbon cloth substrate is negligibly small. In this study, the ternary hybrid nanocomposite RGO-(RuO2/CNCs) is prepared by mixing of 80% of RGO and 20% of (RuO2/CNCs). The final composite contains 80% RGO, 5% CNCs, and 15% RuO2.

The variations in the specific capacitances of aqueous symmetric supercapacitors based on CNCs, RGO, RuO2/CNCs, and RGO-(RuO2/ CNCs) electrodes with an increase in current density values are shown in Fig. 5(b). In general, for supercapacitors, the specific capacitance values tend to decrease with increase in the current density. At lower current densities, electrolyte ions can easily penetrate and access almost all the available pores in the electrode, whereas, at higher current densities, electrolyte accessibility is limited to the electrode surface. In the present study also at lower current densities below 5 A g-1, the specific capacitance decreases with increase in current density. Above 5 A g-1, the specific capacitance is nearly stable. At a constant current density of 1 A g-1, specific capacitances of 127, 166, 321 and 436 F g-1 respectively are obtained for symmetric supercapacitors based on CNCs, RGO, RuO2/CNCs and RGO-(RuO2/CNCs) electrodes. Symmetric supercapacitor based on RGO-(RuO2/CNCs) nanocomposite exhibited excellent rate performance by retaining nearly 92% of the initial capacitance (1 A g-1) at a higher current density of 40 A g-1 (400 F g-1). The rate performance (capacity retention ratio as a function of the current density) of the ternary hybrid nanocomposite is much superior as compared to that obtained for pure RGO based capacitor (~82%of the initial capacitance is retained at a current density of 40 A g-1). By reducing the particle size of nanocrystalline RuO2 in the RuO2/CNCs composite, we are in fact, increasing its specific surface area and providing metal centers for multiple redox reactions. The RuO2/ CNCs act as efficient spacers between individual graphene layers and results in the formation of a highly porous three-dimensional network with easy electrolyte accessibility, leading to the improved rate performance of the RGO-(RuO2/CNCs) nanocomposite.

The cycling stability is a critical performance parameter in determining the use of supercapacitors for practical applications. The cycling stability curves for the symmetric supercapacitors upon 10000 continuous galvanostatic charge/discharge cycles at a constant current density of 5 A/g is shown in Fig. 6(c). At the end of 10000 cycles, the symmetric supercapacitors based on RGO, RuO2/CNCs, and RGO-(RuO2/CNCs) electrodes respectively exhibited 94%, 90% and 93% of their initial capacitance. Metal oxides undergo rapid degradation as compared to nanocarbons upon the cycling process. RuO2/CNCs contains 75% of RuO2, whereas RGO-(RuO2/CNCs) nanocomposite only 15% of RuO2. Hence, the latter exhibits superior stability than the former. The excellent cycling performance of RGO and RGO-(RuO2/CNCs) based symmetric capacitors suggest that these two samples are having high stability and good reversibility upon the charge-discharge process.

Electrochemical impedance spectra or the Nyquist plots for symmetric supercapacitors based on RGO, RuO2/CNCs and RGO-(RuO2/CNCs) electrodes are shown in Fig. 6(d). From the insets, it is clear that each spectrum consists of a semicircle in the high-frequency region and a straight line in the low-frequency region. The X-intercept and diameter of the semi-circle respectively gives the value of the solution resistance (Rs) arising from the uncompensated resistance of the bulk electrolyte solution (0.45 Ω, 1 Ω, and, 0.54 Ω respectively for RGO, RuO2/CNCs, and RGO-(RuO2/CNCs) composite based electrodes) and charge transfer resistance (Rct), respectively. The equivalent circuit for RGO-(RuO2/CNCs) based ideal symmetric supercapacitor is shown as an inset of Fig. 6(d). In the circuit, RS is connected in series with a double layer capacitance (Cd l), and the Cd l is connected in parallel with the Rct and pseudo-capacitance (CPE). Theoretical Nyquist plot corresponding to this circuit should contain a semi-circle at high-frequency region followed by a vertical line within the low frequency region. The deviation of the straight line in the low-frequency region from vertical direction corresponds to the non-ideal pseudocapacitive behavior.

The maximum power density (Pmax) of the RGO-(RuO2/CNCs) based symmetric supercapacitor device is calculated using equation,

 (5)

where  is the initial voltage (here it is 1V), *Rs* is the ESR and *M* is the total mass of active materials in two electrodes (in this case 8 mg) with a cell voltage of 1.0 V. Maximum power density obtained for RGO-(RuO2/CNCs) composite based supercapacitors is 57 kW kg-1.

The energy and power densities were derived from charge–discharge curves at different current densities. The energy (E) and power (P) density values are calculated by taking account of the total mass of material in both electrodes as per the following equations.

 and  (6)

Where ‘’ is the potential window, ‘’is the discharge time of the discharge process and *Cg* is the gravimetric cell capacitance.

The energy density (based on the total mass of active materials in both electrodes) of RGO-(RuO2/CNCs) // RGO-(RuO2/CNCs) symmetric supercapacitor at a power density of 1kW kg-1, is calculated as 14.7 Wh kg-1.

Further improvement in the performance can be achieved by using the asymmetric configuration of electrodes. RGO-(RuO2/CNCs) can be used as the positive electrode (cathode) and pure RGO as the negative electrode (anode). To evaluate the stable electrochemical potential windows of the anode and cathode, comparison of their CV curves in 3 electrode configuration were carried out. The results shown in Fig. 7(a) reveals that RGO-(RuO2/CNCs) and RGO electrodes possess stable voltage windows between 0 and 1 V and between -1 and 0 V, respectively, with respect to the Ag/AgCl reference electrode. RGO-(RuO2/CNCs) electrode exhibits a specific capacitance of 725 Fg-1.Hence, it is expected that RGO-(RuO2/CNCs)//RGO asymmetric hybrid supercapacitor test cell could theoretically achieve a maximum working voltage of 2 V. An asymmetric supercapacitor capable of stable operation in a potential window of 2 Vis constructed with RGO-(RuO2/CNCs) as the cathode (mass loading=2 mg) and pure RGO (mass loading=5.6 mg) as the anode according to the charge balancing principle based on the following equations.

 and  (7)

Where  and respectively are the charges stored in the positive and negative electrodes. The stored charges are proportional to the specific capacitance (C), the potential window (V) and the mass (m) of the electrode, i.e.,  [[30-32](#_ENREF_30)].

Schematic of the asymmetric capacitor is shown in Figure 7(b). CV curves of optimized RGO-(RuO2/CNCs)// RGO asymmetric hybrid supercapacitor at different potential windows at a scan rate of 100mV s-1 are shown in Figure 7(c), which confirm that the device can be safely operated in a potential window of 0 to 2 V. CV measurements were conducted for the fabricated asymmetric supercapacitor at different scan rates 5, 10, 20, 50 and 100 mV s-1 within the potential window of 0 to 2 V and the results are shown in Fig. 7(d). The shapes of CV curves of the capacitors do not change, with the increase of scan rate, implying the excellent electrochemical performance of the device.

Galvanostatic CD curves for the fabricated optimized asymmetric capacitor at different current densities are shown in Fig. 8(a). Nearly triangular shape of the curves indicated the excellent capacitive behavior. A *Cg* of 82 F g-1 is obtained for the asymmetric supercapacitor (*M*= 7.6 mg) at a constant current density of 1A g-1. Variations in gravimetric cell capacitance of the asymmetric supercapacitor and symmetric supercapacitors based on RGO and RGO-(RuO2/CNCs) with the increase in current density are shown in Fig. 8(b). From the graph, it is clear that the gravimetric cell capacitance of the asymmetric supercapacitor is much higher than that of the RGO //RGO symmetric capacitor and lower than that of the RGO-(RuO2/CNCs) //RGO-(RuO2/CNCs) symmetric capacitor at the same current density. The asymmetric capacitor exhibits an excellent rate performance of 90%. Ragone plot of RGO-(RuO2/CNCs)//RGO asymmetric supercapacitor is compared to that of RGO//RGO and RGO-(RuO2/CNCs)//RGO-(RuO2/CNCs) symmetric capacitor.

The asymmetric supercapacitor possesses much higher energy and power densities than the symmetric capacitors. The asymmetric capacitor exhibits a high energy density of 45 Wh Kg-1 at a power density of 1 kW kg-1 and retains an energy density of 41 Wh Kg-1 even at a high power density of 40 kW kg-1(**Fig. S4**). The symmetric supercapacitors based on RGO and RGO-(RuO2/CNCs) could exhibit only 5.5 and 14.7 Wh Kg-1. The performance of the RGO-(RuO2/CNCs) //RGO asymmetric capacitor is much superior to RGO/RuO2// RGO/PANI[[33](#_ENREF_33)], MnO2/Graphene//Graphene [[16](#_ENREF_16)], graphene foam/polyvinyl alcohol /formaldehyde //activated carbon [[34](#_ENREF_34)] , RGO/MnO2/fFWNT // AC/fFWNT [[35](#_ENREF_35)], Co0.5Ni0.5(OH)2/graphene/CNTs// AC/CNTs [[36](#_ENREF_36)], asymmetric capacitors.

The resistive and capacitive behaviors of the fabricated asymmetric supercapacitor is analyzed using the EIS data. The Nyquist plot for RGO-(RuO2/CNCs)//RGO asymmetric supercapacitor is shown in Fig. 8(d), from which the Rs and Rct values are calculated as 0.92 and 0.15Ω respectively. The low value of Rct indicates the presence of large electroactive surface area. The steep rising trend of the imaginary part Z” of the impedance concerning to its real part Z’ of the in the low-frequency region reflects the non-ideal pseudocapacitive behavior of the cell. The inset of Fig. 8(d) shows the frequency response of gravimetric capacitance obtained from EIS measurements for the fabricated asymmetric supercapacitor. The capacitor retains nearly half of its maximum capacitance (@ 0.01 Hz), at a frequency of 1 Hz and in the high-frequency region above 1000 Hz it behaves like a pure resistor. The maximum possible power density of the asymmetric supercapacitor is calculated the Nyquist plot, according to the equation (5). The maximum power density of 143 kW kg-1 is obtained for the asymmetric supercapacitors. The result demonstrates that the RGO-(RuO2/CNCs)//RGO asymmetric supercapacitor is a very promising electrochemical capacitor with both high energy and power densities.

1. **Conclusions**

In summary, we have successfully prepared the RGO based ternary nanocomposite and demonstrated its application as an efficient electrode material for high rate, high energy density supercapacitors. The RGO-(RuO2/CNCs) composite electrode exhibited a high specific capacitance of 436 F g-1 at a constant current density of 1 A g-1 and a high rate performance of 92% at current densities ranging from 1-40 A g-1 in the symmetric two electrode configuration. The asymmetric capacitor fabricated using RGO-(RuO2/CNCs) as the cathode and RGO as the anode exhibited a high gravimetric energy density of 45 Wh Kg-1 at a power density of 1 kW kg-1. Our results provide a rational design strategy for the construction of supercapacitors meeting the requirements of high energy and power densities for advanced energy storage applications.

**Acknowledgements**

Authors thank the Materials Sciences and Technology Division, CSIR NIIST for the help in materials characterization and ‘Mr. Kiran Mohan CSIR-NIIST for TEM measurements. R.B.Rakhi acknowledges the support of Ramanujan Fellowship, Department of Science and Technology (DST), Govt.of India and CSIR-NIIST Thiruvananthapuram, India.

**Appendix A. Supplementary data**

Supplementary data associated with this article is attached as a separate file.

SEM image and EDAX pattern of RGO-(RuO2/CNCs) nanocomposite, TEM and HRTEM images of CNCs, TEM, HTREM images and EDAX pattern of RuO2/CNCs and Ragone plot of the symmetric and asymmetric capacitors.

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**Figure Captions**

1. Schematic of the synthesis of RGO-(RuO2/CNCs).
2. (a) Powder XRD patterns of CNCs, RuO2/CNCs, RGO and RGO -(RuO2/CNCs). (**b)** TGA curves for CNCs and RuO2/CNCs. **(c)** Nitrogen adsorption and desorption isotherms and **(d)** Pore size distributions of CNCs, RuO2/CNCs, RGO and RGO -(RuO2/CNCs).
3. SEM images of (a) CNCs, (b) RuO2/CNCs, (c) RGO and (d) RGO -(RuO2/CNCs)
4. TEM images of (a) G, (b) and (c) RuO2/CNCs, and (d) RGO -(RuO2/CNCs). SAED pattern of RuO2/CNCs is shown as the inset of (c).
5. Cyclic voltammograms of symmetric supercapacitors based on (a) RGO and (b) RGO -(RuO2/CNCs). Galvanostatic charge-discharge curves of symmetric supercapacitors based on (c) RGO and (d) RGO -(RuO2/CNCs).
6. (a) Comparison of cyclic voltammograms at a scan rate of 10 mV/s, (b) variation in the specific capacitance as a function of current density (c) cycling performance and (d) Nyquist plots of the symmetric supercapacitors.
7. Comparison of the CV curves of RGO -(RuO2/CNCs) and RGO at a scan rate of 20 mV s-1 in three electrode configuration, (b) Schematic of the asymmetric capacitor. (c) CV curves of the asymmetric capacitor in different potential windows at a scan rate of 100mV s-1. (d) CV curves of the asymmetric supercapacitor at different scan rates
8. Galvanostatic charge-discharge curves of the asymmetric supercapacitor at different current densities, (b) Variation of gravimetric capacitance as a function of current density and (c) Ragon plots for RGO // RGO, RGO -(RuO2/CNCs)// RGO -(RuO2/CNCs), RGO -(RuO2/CNCs)// RGO supercapacitors. (d) Nyquist plot of the fabricated asymmetric capacitor (Inset shows the variation of gravimetric capacitance as a function of frequency).

**Figures**

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**Figure 1**





**Figure 2**

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**Figure 3**

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**Figure 4**





**Figure 5**



 

**Figure 6**

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**Figure 7**





**Figure 8**

**Table of contents image**

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**Schematic and SEM image of RGO-(RuO2/CNCs) composite and schematic of the RGO-(RuO2/CNCs) //RGO asymmetric capacitor**