Anchoring Samarium Oxide Nanoparticles on Reduced Graphene Oxide for High-Performance Supercapacitor

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Abstract:

We have synthesized Sm_2O_3 nanoparticles (SmNs) and anchored them onto the surface of reduced graphene oxide (RGO) through a self-assembly thereof by utilizing a facile sonochemical procedure. The nanomaterials were characterized by means of powder X-ray diffraction (XRD), Field-emission scanning electron microscopy (FE-SEM), fourier transform infrared spectroscopy (FT-IR) spectra, and X-ray photoelectron spectroscopy (XPS). As the next step, the supercapacitive behavior of the resulting nanocomposites were investigated when used as electrode material, through with cyclic voltammetric (CV), galvanostatic charge-discharge and electrochemical impedance spectroscopy (EIS) techniques. The SmNs decorated RGO (SmN-RGO) nanocomposites were found to possess a specific capacitance (SC) of 321 F g^{-1} when used in a $0.5 \text{ M Na}_2\text{SO}_4$ solution as an electrolyte, in a scan rate of 2 mV s^{-1} . The SC of the SmN-RGO based electrodes were also found to be 268 F g^{-1} at a current density of 2 A g^{-1} through galvanostatic charge-discharge tests. The outstanding properties of the SmN-RGOs were attributed to synergy of the high charge mobility of SmNs and the flexibility of the sheets of RGOs. Additionally, the nano-composite revealed a unique cycling durability (maintaining 99 % of its SC even after 4000 cycles).

Keywords:

Samarium oxide, Graphene, Nanocomposites, Supercapacitor, Energy storage

1. Introduction

Using high-tech energy storage devices such as supercapacitors, is one of the strategies adopted to meet the incremental demand for energy, in the modern world [1]. These devices enjoy the advantage of considerable energy density, the ability of fast charge/discharge, and long life cycles over the conventional capacitors [2-4]. Function of supercapacitors falls into two mechanisms, and the devices have hence been divided into two major categories, i.e. pseudo-capacitors and electrical double-layer capacitors (EDLCs).

In the case of pseudo-capacitors, the electrode materials used to construct the electrodes include oxides of noble and transition metals or conducting polymers, while EDLCs mainly use carbonaceous materials such as carbon nano-tubes (CNTs) or graphene to the same end [4, 5]. The latter group of electrode materials constitute a class with unique properties including very high conductivity, thermal and chemical stability, as well as considerable surface area [6].

The fact that graphene can be produced from reduced graphene oxide (RGO) via low-cost procedures, has boosted the interest placed on this material [7]. A further incident that has attracted a great deal of interest towards this material is the advent of decorating RGO with various nano-materials. The resulting hybrid nano-materials have a set of various properties that can be fine-tuned by altering the loading degree, as well as the nano-material loaded on the RGO sheets [7-15]. A group of materials used for the decoration of RGO are metal oxides like MnO_2 , Mn_3O_4 , RuO_2 , CeO_2 and SnO_2 , which result in avoiding losing the surface area of RGOs, which is the result of the restacking of the graphene sheets. Hence graphene sheets loaded with such nano-materials can lead to increased accessibility of the graphene surface through the spacing function of such nano-particles between the graphene sheets [16, 17]. The open spaces created among the sheets this way, greatly drops the internal resistance of the material, facilitating the diffusion of the electrolytes throughout the electrodes based on such materials [18]. As a result of all these modifications on carbonaceous materials, the energy density and capacitance of supercapacitors has been found to greatly increase [2, 4, 17, 19-21].

Lanthanoid oxides or in other words rare earth oxides (REOs), have recently attracted a great deal of attention and scientific endeavour due to their widespread applications

including ion glass industries, heterogeneous catalysis, electronics and fuel cells [22-26]. REOs are known to undergo two distinct types of chemical processes, i.e. redox and acid-base reactions[22, 27], and given their redox properties [22], REOs constitute a set of potential candidates for pseudo-capacitors.

The lanthanoid used in this research i.e. samarium adopts both +2 and +3 oxidation states [22, 28]. The focus of the current work is to introduce a facile, green procedure for the preparation of Sm_2O_3 in the form of nano-particles and using them to construct Sm_2O_3 nanoparticles decorated RGO (SmN-RGO) nanocomposites through mild sonochemical conditions. Given that the size of the Sm_2O_3 falls in the nanometer scale and hence the increased surface area, its redox activity is greatly enhanced. To more clearly understand the influence of the composition of the nanomaterial on the supercapacitive behavior of the material 3 distinct compositions with various Sm_2O_3 /RGO ratios were prepared and investigated.

2. Experimental

2.1. Materials

Samarium(III) nitrate hexahydrate ($\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$), poly(tetrafluoroethylene) (PTFE), hydrazine hydrate (N_2H_4), Graphite flakes (cat #332461), and ammonium hydroxide (NH_4OH) were purchased from Sigma-Aldrich Co. Potassium permanganate (KMnO_4), sodium sulfate (Na_2SO_4) and hydrogen peroxide (H_2O_2) were purchased from Merck Chemical Co. Phosphoric acid (H_3PO_4), sulfuric acid (H_2SO_4) and hydrochloric acid (HCl) were all purchased from Mojallali Chemical Co. Acetylene black (>99.9%, S.A. $80 \text{ m}^2\text{g}^{-1}$) was purchased from Alfa Aesar Co. All reagents were used without any further modification.

2.2. Preparing the SmN-RGO nano-composites

The SmN–RGO hybrid material was prepared through a facile sonochemical routine previously reported in other works [16, 21]. The method generally involves the synthesis

of Sm_2O_3 nanoparticles (SmNs); depositing the SmNs on the graphene oxide (GO) sheets; and finally reducing the loaded GO to RGO (Scheme 1).

In practice a 32% ammonia solution, was slowly added into a solution of $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ under sonication in an ultrasonic bath (FALC instruments ultrasonic) for 60 min. Then the resulting suspension was add-mixed with a suspension of GO and the sonication was started and continued for 20 min. This was intended to anchor the nano-particles onto the GO sheets, which was followed by the final step of reducing GO to RGO through the addition of the reducing agent (i.e. N_2H_4). This way a black precipitate was formed which was subsequently dried at 60°C for one day. The material formed under these conditions shall be referred to as SmN-RGO throughout the text. It is noteworthy that both pure Sm_2O_3 and RGO were prepared through the same procedure (i.e. GO was prepared starting from graphite flake powder using the Tour's method [29]). Table 1 presents a summary of the details of the Sm_2O_3 / RGO ratios in the SmN-RGO samples.

Scheme 1.

2.3. Characterizations

The crystallinity of the samples was evaluated through X-ray diffraction (XRD) using a Philips PW-1730 X-ray diffractometer equipped with Cu K_α radiation ($\lambda = 1.5405\text{\AA}$). The Field-emission scanning electron microscopy (FE-SEM) was conducted using a Zeiss SIGMA VP system with gold coating, in order to study the size and morphology of the products. The Fourier transform infrared spectroscopy (FT-IR) spectra, were acquired using a BRUKER EQUINOX 55 spectrophotometer. Furthermore, X-ray photoelectron spectroscopy (XPS) measurement was performed on a Perkin Elmer PHI 6000C ECSA system with monochromatic Al KR (1486.6 eV) irradiation.

2.4. Electrochemical studies

Part of the electrochemical measurements were performed on an electrochemical workstation (PGSTAT30, Autolab, Netherland) using three-electrode and two-electrode

mode in 0.5 M Na₂SO₄ aqueous solution. The working electrodes were prepared for the electrochemical tests by preparing a mixture of the produced materials (i.e. pure RGO and Sm₂O₃, as well as, SmN-RGO nanocomposites) with acetylene black, and poly(tetrafluoroethylene) at a 80:15:5 mass ratio in ethanol. The resulting uniform paste was then pressed on a current collector, which was a piece of stainless steel, in order to for the electrodes. To this end about 1 mg of the electroactive material and a 1 cm² current collector were used. Eventually the electrodes were dried in a vacuum oven, at 80°C for 4h. The electrodes manufactured under these conditions shall be referred to as SmRGO throughout the text. The reference and counter electrode were Ag/AgCl and platinum electrode, respectively. A three-electrode cell system was used to evaluate the electrochemical performance by electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV) and the continuous cyclic voltammetry (CCV). A home-made device was used to perform the CCV measurements as described earlier [16, 30, 31].

Table 1.

3. Results and discussion

3.1. Nanocomposite characterization

3.1.1. XRD analysis

Figure 1 shows the XRD patterns of GO, RGO, Sm₂O₃ and the Sm₂O₃ –RGO nanocomposites. The most evident peak in the XRD pattern of GO happened at $2\theta = 12.2^\circ$, which was attributed to the (001) reflection of graphite oxide [8]. This was not observed in the case of RGO, which is a sign of the complete reduction of GO using hydrazine hydrate [8]. Additionally, the RGO pattern contains two diffraction peaks around 25° and 43° , which can be attributed to the (002) and (100) planes of the graphite-like structure [12, 21]. The XRD pattern of the Sm₂O₃ showed a broadening, which was attributed to the fine dimensions of SmNs, and their low crystallinity. The same pattern was observed for the SmN–RGO nanocomposites, reflecting the presence of the SmNs on the surface of the RGO.

Fig. 1.

3.1.2. TEM / FE-SEM studies

Fig. 2a indicates a layered and wrinkled morphology for the pure RGO. The FE-SEM image of the SmNs (Fig. 2b) reveals that the nanoparticles are aggregated with a grain size about 20 nm. An almost regular distribution of SmNs can be seen in the SmN-RGO2 nanocomposite (Fig. 2c-d). This confirms the good combination between the RGO and SmNs. The morphology of the SmNs does not change in the pure and composite forms even though the SmNs underwent some aggregation in pure form (Fig. 2b), which implies that the formation of the nanocomposites prevented the agglomeration of the SmNs and also that the nanoparticles prevent the restacking of the RGO sheets [21].

Fig. 2.

3.1.3. FT-IR study

Fig. 3 illustrates the FT-IR spectra of the GO, RGO, Sm_2O_3 and SmN-RGO nanocomposites. The signals at 1735 cm^{-1} and 1050 cm^{-1} , in the FT-IR spectra of the GO was attributed to the stretching of C=O and C-OH on COOH groups. The band at 1621 cm^{-1} was assigned to the bending vibrations of the surface-adsorbed water molecules as well as the contribution of the sp^2 bonds. Also the deformation and stretching vibrations of the -OH groups were considered as the origin the peaks at around 1397 cm^{-1} and 3400 cm^{-1} respectively. Furthermore, a band at 1225 cm^{-1} is corresponded to the epoxy groups. In the FT-IR spectra of RGO and SmN-RGO nanocomposites, the characteristic absorption band of GO at 1735 cm^{-1} is vanished, indicating the successful reduction of GO. Furthermore, these spectra exhibit the characteristic band of graphene around 1585 cm^{-1} . [21] The FT-IR spectrum of Sm_2O_3 exhibits a band at 680 cm^{-1} which has been assigned to a deformation mode of the Sm-O-H of the $\text{Sm}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ phase. Furthermore, a shoulder at 1625 cm^{-1} corresponding to the bending mode of molecular water can be seen in this spectrum [32]. The peak at 1384 cm^{-1} in the spectra of Sm_2O_3 and SmN-RGO nanocomposites is assigned to the adsorbed nitrosyl $(\text{N-O})^-$ [25]. In the spectra of SmN-RGO nanocomposites, the band around 590 cm^{-1} can be assigned to the Sm-O vibration of the strong interaction between SmNs and RGO which can describe anchoring of nanoparticles on RGO.

Fig. 3.

3.1.4. XPS study

The SmN-RGO2 nanocomposite is also studied by the X-ray photoelectron (XPS) technique. The wide range XPS survey spectrum of the synthesized sample shown in Fig. 4a indicates no impurities in this nanocomposite. The deconvoluted Sm 3d spectrum (Fig. 4b) consists of two intense bands 1087.3 eV and 1111.4 eV corresponding to Sm^{3+} and a broad peak with low intensity centered 1099.1 attributed to the Sm^{2+} component, suggesting a small amount of oxygen vacancy [33]. The O1s spectrum as shown in Fig. 4c was fitted by three components. The weak peak at 534.2 eV may be attributed to the oxygen of OH groups on the particle surface. The main peak at 531.6 eV could be assigned to the oxygen of Sm^{3+} -O groups, and another weaker peak with higher binding energy of 529.3 eV was assigned to the oxygen of Sm^{2+} -O groups, which are related to the oxygen in the crystal lattice of Sm_2O_3 . The coexistence of these peaks reveals the presence of Sm in two different ionic states; therefore, oxygen vacancy in the crystal lattice of Sm_2O_3 is helpful for transferring the charge [34]. As shown in Fig. 4d, the curve fitting yields four components at C-C (sp^2 carbon, approximately 284.4 eV), C-O (hydroxyl and epoxy, approximately 286.5 eV), and C=O (carboxyl, approximately 288.2 eV), respectively [12, 35].

Fig. 4.

3.2. Electrochemical studies

3.2.1. CV and specific capacitances

The supercapacitive behavior of the RGO, SmN, and SmN-RGO nanocomposite electrodes (i.e. SmRGO1, SmRGO2 and SmRGO3) were monitored using a 3-electrode system and a 0.5 M Na_2SO_4 solution as the electrolyte, under ambient. CV was further used to evaluate the current responses of the materials under the mentioned conditions. The results obtained for the SmN and SmN-RGO electrodes illustrated by Fig. 5, based on which the corresponding specific capacitance (SC) values were calculated from using the equation below [36];

$$SC = \frac{1}{v(V_c - V_a)} \int_{V_a}^{V_c} I dV$$

where v is the potential scan rate (mV s^{-1}), V_c and V_a determine the potential range and I denote the response current (mA g^{-1}) based on the mass of the electroactive material.

Fig. 5.

Fig. 5a contains the CVs obtained for the RGO, SmN and SmN-RGO electrodes with various ratios in a 0.5 M Na_2SO_4 solutions at 50 mVs^{-1} . As can be seen in this figure, the rectangular area of the CV loop in the SmRGO2 is significantly larger than that of RGO, SmN, SmRGO1 and SmRGO3 electrodes. The SC values of the RGO, SmN, SmRGO1, SmRGO2 and SmRGO3 electrodes were calculated as 76 F g^{-1} , 87 F g^{-1} , 180 F g^{-1} , 227 F g^{-1} , and 196 F g^{-1} at a scan rate of 50 mV s^{-1} . This can be the result of both the synergistic effects between the components as well as the smaller particles present on the surface of the electrodes. The latter, naturally leads to high specific surface areas, which can in turn enhance the number of active sites available, increasing the amount of energy that supercapacitor electrodes can store [37]. Fig. 5b, 5c, 5d and 5e illustrates the CV curves of the SmN, SmRGO1, SmRGO2 and SmRGO3 at the scan rates of 5, 10, 20, 30, 50, 75 and 100 mV s^{-1} , respectively. All the CVs of the SmRGOs are made of two approximate mirror images with respect to the zero-current line. The fast current response to reversing the voltage at the end of each potential scan proves the ideal pseudo-capacitive nature of the composite. It can be clearly observed that in the case of the SmRGO2, the area of the CVs is significantly larger.

Finally, Fig. 5f illustrates SC vs. scan rate behavior of the SmN and SmRGOs. It is clear that the SC of SmN and SmN-RGO2 drops from 151 and 321 to 63 and 151 F g^{-1} , respectively, as a result of increasing the scan rate. Lower scan rates allow the Na^+ or H^+ ions to thoroughly diffuse into the pores in the electrode material, virtually increasing the surface available for redox reactions, while at higher scan rates this is limited to the outside surface of the electrode material, as a result of which the SC values decrease by increasing the scan rate [12, 16].

3.2.2. CCV

To evaluate the cycling stability of RGO, SmN, and SmRGOs, CCV analysis were also conducted at 200 mV s^{-1} for 4000 cycles [16, 31], and the results (Fig. 6) show that among the different SmRGOs, SmRGO2 revealed exceptionally high cyclic stability. The cyclic stability of

this electrode increased about 5.7% after 300 cycles and then showed a 1.0% decrease after 4000 cycles. Similar to SmRGO2 the cyclic stability curve of SmRGO3 first showed a slight increase after 1000 cycles, and finally decreased to 97.6% of the initial value after 4000 cycles. The initial increase could be the result of the activation of the electrode material, which increases the number of available active sites.

In the case of the RGO, SmN, and SmRGO1 electrodes the cyclic stability decreased by 3.9%, 23.6% and 4.2% after 4000 cycles. The results indicate that the RGO content of the electrodes considerably influences the cyclic stability of the electrodes, and hence the application of the optimal amounts of RGO is crucial for improved cyclic stability. Further it is evident that the considerable stability of RGO-based electrodes, even at high scan rates makes them a suitable candidate for applications requiring fast charging. Fig. 6b, 6c and 6d illustrates three-dimensional (3D) CCVs, which was performed at a scan rate of 200 mV s⁻¹. In these three 3D-plots, the changes in the CVs over number of cycles are more noticeable.

Fig. 6.

3.2.3. Charge/discharge

Galvanostatic charge/discharge analyses were also conducted to evaluate the supercapacitive performance of the electrodes. For this purpose, a two-electrode system was used. Fig. 7a illustrates the charge/discharge curves of the RGO, SmN, and SmRGO electrodes at the current density of 2.0 Ag⁻¹. The results reveal that the curves of SmRGOs to be triangular, linear, symmetric and very sharp. Equal charge/discharge durations for each electrode indicate reversible behavior, high columbic efficiency, and an ideal capacitor performance. The SC values were also calculated using the charge/discharge data by means of the following equation:

$$SC = \frac{I\Delta t}{\Delta V}$$

where I is the charge/discharge current (A), Δt is the discharge time (s), and V is the potential drop during discharge (V).

Fig. 7.

In the case of the SmRGO2 a specific capacitance of 268 Fg^{-1} was achieved at 2 Ag^{-1} , which further proved to be the largest value among all the electrodes. Fig. 7b illustrates the charge/discharge curves of this electrode in the -0.8 to 0.2 V window at various current densities from 2 to 32 A g^{-1} . The equilateral triangular curves in all cases indicate the ideal capacitive behavior and reversibility of the material in the charge/discharge processes, which was attributed to the considerable electrical conductivity of RGO (due to the presence of SmN), and the rapid redox reactions stemming from the facilitated charge transport from Sm_2O_3 as a function of uniform distribution of SmN on the RGO sheets [38].

According to the results acquired from CV, charge/discharge and CCV, supercapacitive performance of SmRGO2 electrode is much better compared to the other works presented in Table 2. As can be seen in Table 2, the maximum SC and stability of SmRGO2 electrode are higher than those of graphene/metal oxide composites that have been investigated in aqueous electrolytes so far.

Table 2.

The superior performance of the SmRGO2, in comparison with the other electrodes was also verified by the Ragone plot as shown in Fig. 7c. The energy and power densities, required for this plot, were acquired from charge/discharge analysis at the various current densities and the highest energy density (i.e. 38.1 W h Kg^{-1}) was observed for the SmRGO2 at the power density of 500 W Kg^{-1} . The value was found to be considerably higher than those reported for the same electrode in the literature [44-46]. Upon increasing power density, the energy density values of this electrode decreased lower sharply than the other composite electrodes, indicating the higher available active sites in SmRGO2. Based on the energy and power densities the SmN-RGO composites were considered as suitable materials for supercapacitor electrodes.

3.2.4. EIS studies

To compare the internal resistance of the electrode materials with the external resistance between the electrode and electrolyte, EIS evaluations were also conducted. The EIS measurements of SmRGOs were performed at open circuit potential (OCP) in the range of $0.1 - 10^5 \text{ Hz}$ (Fig. 8). The charge transfer between electrode and electrolyte leads to semicircular patterns in the

Nyquist plot at the high frequency region. This is followed by a tail caused by the diffusion of the ions into the electrode, at lower frequencies. Alternatively, it can be said that the electrochemical reaction impedance influences the size of semicircle, in a way that smaller semicircle radius translates to smaller charge transfer resistance [47]. The EIS curves were analyzed through complex nonlinear least square (CNLS) fitting method [48], for an equivalent circuit according to Fig. 8 (inset), which can be seen as the combination of five elements of R_s , R_{ct} , C_{dl} , Z_W , and C_F . (R_s : the internal resistance, the sum of the intrinsic resistance of the active material, resistance of the bulk electrolyte, and the ionic resistance of the electrolyte at current collector/electrode interface [49]; Z_W : Warburg resistance, indicating the frequency dependence of ion diffusion/transport to the surface of the electrode [50]; R_{ct} : the electrode/electrolyte interfacial charge transfer resistance; C_{dl} : the electrical double layer capacitance at the electrode/electrolyte interface; and C_F : pseudo-capacitance of the faradic reaction).

The values obtained for the equivalent circuit are given in Table 3, which shows that R_{ct} of SmRGO2 is less than those of the other composite electrodes. Low R_{ct} indicates that the electrochemical reaction is more facile at the electrode/electrolyte interfaces. Similarly, as seen in Table 3, the SmRGO2 was concluded as being superior, in terms of the electrochemical performance, to the other composite electrodes. The highest values of electrical double layer capacitance (C_{dl}) and faradic pseudocapacitor (C_F) are corresponded to the SmRGO2. Also, SmRGO2, further proved to have a more ideal Warburg resistance (the closeness of the line to verticality is indication of the fact that the electrode is closer to an ideal capacitor) [51]. The EIS actually revealed that the synergy between the SmN and RGO sheets reached its peak at the composition of the SmRGO2, which was further approved by CVs and chronopotentiograms.

Fig. 8.

Table 3.

4. Conclusion

Samarium oxide/RGO nanocomposites, were prepared through a simple sonochemical procedure, and the evaluation showed that the presence of RGO led to improved conductivity by declining the ionic mass-transfer resistance. Experiments revealed that SmN-RGO nanocomposite

electrodes reveal better behaviors as opposed to those based on pure RGO or Sm_2O_3 in terms of SC, stability, and energy density. It was also concluded that a composition of 1:1 wt. of Sm_2O_3 to RGO (referred to as SmN-RGO2) leads to the best supercapacitive performance, with an SC of approximately 321F g^{-1} , at a scan rate of 2 mV s^{-1} , which is much enhanced with respect to pure RGO and Sm_2O_3 electrodes. The stability of the nanocomposite electrodes was assessed by CCV, at 200 mVs^{-1} , which indicated that the SC of the SmN-RGO2 based electrodes remained at approximately 99.0% of its initial value, after 4000 cycles. EIS and galvanostatic charge/discharge evaluations confirmed these findings and hence, the optimal SmN-RGO nanocomposites were suggested as a promising candidate for use in the construction of high performance super-capacitor electrodes. The proposed synthesis, also seems to be extendable to other metal oxides and carbonaceous materials such as CNTs and mesoporous carbon, which can be used in super-capacitor technologies.

Acknowledgements

The financial support of this work by Iran National Science Foundation (INSF) and University of Tehran is gratefully acknowledged.

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Table 1. Theoretical $\text{Sm}_2\text{O}_3/\text{RGO}$ ratios in various SmN–RGO compositions applied in related electrodes.

Electrode	Nanocomposite	Sm^{3+} (mmol)	Theoretical mass ratio $\text{Sm}_2\text{O}_3/\text{GO}$
SmRGO1	SmN-RGO1	0.35	2/1
SmRGO2	SmN-RGO2	0.175	1/1
SmRGO3	SmN-RGO3	0.0875	1/2

Table 2. Comparison between supercapacitive behavior of $\text{Sm}_2\text{O}_3/\text{RGO}$ and some reported metal oxide/graphene composite electrodes.

Composite	Electrolyte	Potential window (V)	Specific capacitance	Cycling stability	Ref.
$\text{Yb}_2\text{O}_3/\text{RGO}$	0.5 M Na_2SO_4	-0.9 - 0.1	240 F g^{-1} (2 mV s^{-1})	96.5% (4000 cycles)	[12]
CeO_2/RGO	0.5 M Na_2SO_4	-0.8 - 0.6	211 F g^{-1} (5 mV s^{-1})	105.6% (4000 cycles)	[16]
$\text{Fe}_3\text{O}_4/\text{RGO}$	0.5 M Na_2SO_4	-0.8 - 0.2	271 F g^{-1} (2 mV s^{-1})	93.8% (4000 cycles)	[35]
$\text{Co}_3\text{O}_4/\text{RGO}$	6.0 M KOH	-0.6 - 0.55	291 F g^{-1} (1 A g^{-1})	90.0% (1000 cycles)	[39]
$\text{Fe}_2\text{O}_3/\text{RGO}$	3.0 M KOH	-1.0 - 0.0	300 F g^{-1} (5 mV s^{-1})	75.0% (5000 cycles)	[40]
NiO/RGO	6.0 M KOH	-0.4 - 0.5	461 F g^{-1} (0.2 A g^{-1})	74.5% (5000 cycles)	[41]
MnO_2/RGO	0.5 M Na_2SO_4	-1.0 - 0.8	265 F g^{-1} (1 A g^{-1})	93.8% (4000 cycles)	[42]
ZnO/RGO	6.0 M KOH	-0.6 - 0.6	230 F g^{-1} (5 mV s^{-1})	89.8% (100 cycles)	[43]
$\text{Sm}_2\text{O}_3/\text{RGO}$	0.5 M Na_2SO_4	-0.8 - 0.2	321 F g^{-1} (2 mV s^{-1})	99.0% (4000 cycles)	This Work

Table 3. R_s , C_{dl} , R_{ct} , Z_w , and C_F values calculated through CNLS fitting of the experimental impedance spectra for the given equivalent circuit.

	SmRGO1	SmRGO2	SmRGO3
$R_s(\text{Ohm})$	1.22	1.09	1.22
$C_{dl}(\text{mF})$	1.02	1.1	0.79
Z_w	0.18	0.21	0.16
$R_{ct}(\text{Ohm})$	3.11	1.83	2.16
$C_F(\text{mF})$	218	341	290

Figures Legend

Scheme 1. Schematic presentation of procedure for the synthesis of SmN–RGO nanocomposite.

Fig. 1. X-ray diffraction patterns of RGO, Sm₂O₃, and SmN–RGO nanocomposites.

Fig. 2. a and b) FE-SEM images of RGO and Sm₂O₃, c and d) TEM and FE-SEM images of SmN-RGO2.

Fig. 3. FT-IR spectra of GO, RGO, Sm₂O₃ and SmN–RGO nanocomposites.

Fig. 4. XPS spectra of SmN–RGO2 nanocomposite.

Fig. 5. (a) The cyclic voltammograms of the SmN and SmN-RGO electrodes with various ratios at 50 mV s⁻¹, (b) CVs of the SmN-RGO electrodes containing various amounts of RGO (at 50 mV s⁻¹), (c) CVs of an SmN-RGO electrode at various scan rates in the range of 10-200 mV s⁻¹, and (d) Changes in the SC values vs. the scan rate.

Fig. 6. (a) Changes in the specific capacitance of the RGO, SmN and different SmRGOs as a function of number of cycles, at 200 mV s⁻¹. 3D-CCV curves obtained at 200 mV s⁻¹ for (b) RGO, (c) SmN and (d) SmRGO2 electrode.

Fig. 7. (a) Charge/discharge curves of RGO, SmN and different SmRGOs at a charge/discharge current density of 2.0 A g⁻¹, (b) charge/discharge curves of the SmRGO2 at various current densities in the range of 2-32 Ag⁻¹, (c) the Ragone (power density vs. energy density) plot of the SmN and SmRGOs with different compositions (The energy and power density data were derived from the charge/discharge curves at various current densities).

Fig. 8. Nyquist plots of the impedance spectra of different SmRGOs at OCP in the range of 0.1 – 10⁵ Hz.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8

Scheme 1