Amorphous Carbon Nanotubes—Nickel Oxide Nanoflower Hybrids: A Low Cost Energy Storage Material

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ABSTRACT: Amorphous carbon nanotubes (a-CNTs) have been synthesized by a simple low-temperature process and have been grafted with chemically synthesized nickel oxide microflowers with different concentrations. The phase and morphology of the as-prepared pure and hybrid samples were characterized by X-ray diffraction and field emission scanning and transmission electron microscopes. Thermal properties of the samples were estimated by using thermal gravimetric and differential thermal analysis. The optical properties of the sample were characterized by UV–vis spectroscopic, Raman spectroscopic, and Fourier-transformed infrared spectroscopic analysis. The electrochemical performance of all hybrid samples has been done in detail for different scan rates as well as from charge–discharge analysis. It has been seen that because of the nickel oxide grafting, the electrochemical performance of pure a-CNTs gets enhanced significantly. The value of the specific capacitance of the hybrid comes out to be around 120 F/g for the best sample, which is almost 12 times higher compared to that of the pure a-CNTs. The result has been explained in terms of change in effective surface area as well as change in conductivity of the hybrid samples.

1. INTRODUCTION

The exploration of defects into various applications nowadays becomes an important challenge as well as a great opportunity in the field of nanoscience and technology. On the basis of this idea, the concept of amorphous carbon nanotubes (a-CNTs) becomes fascinating after the crystalline counterpart of the materials being discovered in the year of 1991 by Iijima.1,2 Apart from the scientific interest, the concept of a-CNT is interesting in regard to the cost effectiveness, simplicity, as well as high yield of the material; thus, it can be an important part of nanotechnology as well.

It is an established fact that CNT is an excellent material that can be used in various applications, including mechanical, electrical, electronic, medical, coating, and many others.3–6 Moreover, in all of these fields, systematic efforts are being made to improve the property of the pure CNT by hybridizing it with different materials, like metal, semiconductor, as well as polymers.7–9 These established facts propelled the researchers to explore the amorphous analogue of CNTs in all of these fields and optimize the performance by suitable functionalization or hybridization.10 Few of our previous works report several such applications of a-CNTs and related hybrids in different fields.11–13

A very important application of carbon nanomaterial is that it can be used as a supercapacitor, thus helping in the concept of developing alternative energy sources.14 The application is rather important nowadays due to the crisis of conventional fossil fuel energy, and it is thus very important to focus on the development of renewable and sustainable energy.15 This need propels the current researchers to focus into the field of electrochemical capacitors as the promising candidate regarding energy sources. This interest exists because of several facts, like long life stability, high specific capacitance, high energy, and power density. For further classification of the electrochemical capacitor, it should be noted that electrical double layer capacitor (EDLC) stores charges on the basis of the electrostatic charge storage mechanism whereas supercapacitors are governed by chemical redox reactions. Generally, the transition materials serve as good supercapacitor materials whereas carbon materials with their high surface area are considered to be a good EDLC material.

There are reports of supercapacitive behavior of CNT or graphene and related hybrids with different metal oxides as well

Received: April 24, 2018
Accepted: June 1, 2018
Published: June 12, 2018

DOI: 10.1021/acsomega.8b00798
ACS Omega 2018, 3, 6311−6320
as polymers. For example, Ma et al. reported a very high capacitance value for nickel cobalt hydroxide and reduced graphene oxide hybrid nanolayers for high-performance asymmetric supercapacitors with remarkable cycling stability.16 Mondal et al. also reported the high-capacitance values for multiwall carbon nanotube—nickel cobalt oxide hybrid structure as high-performance electrodes for supercapacitors and lithium-ion batteries.17 Dai et al. reported that cobalt sulfide/carbon nanotube hybrid can be an excellent candidate for storing energy electrochemically.18 Gu et al. reported high-performance all-solid-state asymmetric stretchable supercapacitors based on wrinkled MnO2/CNT and Fe3O4/CNT macrofilms.19 However, all of these reports involve crystalline phase of CNTs and so far the authors are concerned there are no reports regarding the supercapacitor behavior of a-CNTs and related hybrids except few of authors own works published previously,20–22 where a-CNT—copper, a-CNT—manganese oxide, or a-CNT—MnO2—pyrrole hybrid system shows good capacitive property.

As mentioned before, although there are reports of better electrochemical performance of CNT—NiO hybrids, all of these systems are associated with the crystalline CNTs that are costly, hard to develop, and yield is less, which makes them not very suitable for real industry-scale application. Especially, although there are reports of large-scale production of crystalline CNTs that satisfy industry needs, the associated making cost and complexity of the procedure do not encourage the technologists much to proceed further.23–26 For instance, Wang et al. reported the large-scale production of CNT via chemical vapor deposition at much elevated temperatures, as high as 700 °C, with external catalyst.24 Pirard and co-worker followed the same method with additional use of continuous inclined mobile-bed rotating reactor.25 Logeswari et al. reported an efficient catalyst for large-scale production of CNTs, but there also the process needed temperature as high as 800 °C.26 Kim et al. reported the large-scale production of CNTs by evaporating carbon black with introduction of thermal plasma,27 and thus again cost optimization is not satisfactory. Moreover, in all of these cases, being inert for crystalline CNTs’ external acid treatment is necessary, which adds even more cost to system development. However, our system uses a-CNTs, which are cost effective and easy to synthesize with very high yield, thus having the potential for industrial scale use.

Keeping this in mind, here, nickel oxide nanostructure has been chosen for hybridization. It is noteworthy that nickel oxide is another transition-metal oxide that already has established itself as a potential candidate for being used as energy storage material. There are reports of nickel oxide being anchored onto the walls of CNTs and the composites being used as supercapacitor materials, as mentioned before, but the literature remained completely silent regarding the supercapacitive performance of a-CNT—NiO composites.

Thus, here, we have reported for the first time the synthesis of the NiO microflower-decorated a-CNTs and also studied the electrochemical performance of the hybrids in detail.

It should also be noted that this is the first report regarding the electrochemical performance a-CNT—NiO hybrids and thus there is plenty of scope to optimize the performance of the system. In this way, the present work has significant importance in view of the modern energy storage technology.

2. RESULTS AND DISCUSSION

2.1. X-ray Diffraction (XRD) Analysis. Figure 1 shows the XRD pattern of all pure and hybrid samples within the range of 2θ = 20–70 °C with normal θ–2θ scanning. One can see that there are several distinct peaks for the hybrid samples centering around 36, 42, and 62° that are characteristics of (111), (200), and (220) planes of cubic NiO, respectively.

Also, it can be seen that for the pure a-CNTs, there are two broad humps at 26° and 42°. These two are characteristics of (002) and (110) planes of hexagonal graphite phase. It is worth mentioning that unlike the crystalline phase of CNTs, there exist only broad humps at the particular position mentioned, before which are the characteristics of the amorphous CNT where only a short-range ordered periodicity exists. Also, because the synthesis process yields of a-CNTs as well as NiO are not very high, all samples have the poor crystallinity.

It should also be noted that because of the thick coating, hybrid samples show no signs of carbon-related peak at 2θ = 26°. For the other peak at 42°, it can be seen that the position of carbon- and NiO-related peak is almost the same.

2.2. Microscopic Study. Figure 2a–f shows the field emission scanning electron microscopy (FESEM) images of all a-CNTs and hybrid samples S1 and S2 with different magnifications. It is seen that a-CNTs with one-dimensional tubular structure with a diameter of around 120 nm and length of few micrometers have been formed. The structure has been formed uniformly over a large area. It is also seen that the walls of the as-synthesized a-CNTs are rather rough and they are in bundle form, which is mainly due to the strong intertube van der Waal interaction.

In micrographs of both the hybrid samples, one can see the flowerlike NiO structures with dimensions of around 1 μm and the thickness of the individual petal is no more than 10–20 nm. The length and breadth of the petals are around 150 nm each. It is to be noted that the density of the flowers is much higher in the case of sample S2 compared to that of S1. This is because of the fact that the amount of Ni precursor is higher for the synthesis of S2.

From the transmission electron microscopy (TEM) image (Figure 3a,b), the flake-like nanostructure can clearly be seen; however, the entire flowerlike structures were broken mainly due to ultrasonication as well as due to collision with high-energy electron beam during recording. The flakes can be seen
in a wrinkled form and the dimension of individual flakes is around 200 nm, thus supporting the FESEM information.

2.3. Optical Study. Figure 4 shows the Fourier-transform infrared spectroscopy (FTIR) spectra of both S1 and S2 with those of pure a-CNTs shown in the inset. It is seen that both S1 and S2 have peaks centering around 590 and 1625 cm\(^{-1}\). Apart from this, there are three bands between 990−1208, 2835−2985, and 3200−3690 cm\(^{-1}\), of which the middle band is the signature C−H\(_n\) band and the band between 3200−3690 cm\(^{-1}\) is associated with O−H bond. The peak at 1625 cm\(^{-1}\) is the signature of C≡C bond. The peak at 590 cm\(^{-1}\), which is absent in the FTIR spectra of a-CNTs, may be due to Ni−O stretching vibration. The broad band between 990−1208 cm\(^{-1}\), which is also absent in the FTIR spectra of a-CNTs, is due to overlapping of different bonds like C≡C, C−C stretching, and C−N stretching. The FTIR spectrum is kind of an indirect proof of a-CNTs being covered with NiO.

The Raman spectra of both the hybrid samples has been shown in Figure 5, with that of pure a-CNTs shown in the inset. It is seen that for pure a-CNTs, there are two sharp peaks at 1368 and 1574 cm\(^{-1}\). These two are the very well-known D and G bands of carbon, as reported in our previous work, with all other calculated parameters. The hybrid samples due to dense coating of NiO show no such signature, instead two new peaks can be seen around 562 and 1080 cm\(^{-1}\). These two peaks are the signature of 1 photon LO and 2 photon 2LO mode of the nickel oxide. However, it is rather surprising that although the relative percentage of Ni precursors is higher in sample S2, the intensity of the NiO-related peak is higher in sample S1.
The transmittance and absorbance spectra of both the samples S1 and S2 have been shown in Figure 6a,b, with the corresponding Tauc plot shown in the inset of Figure 6a. Before recording the spectra, certain amounts of both the samples were dispersed into ethanol and the dispersion was taken for measurement where the pure ethanol was used as background. It is seen that there are marked differences in spectra of both samples; sample S2 has much higher transmittance compared to that of sample S1, whereas in the absorbance spectra, the trend is reversed, as expected. Also, another marked difference is that for S2, the falling of transmittance is rather sharp compared to that for S1. This is because of the fact that our NiO is crystalline unlike a-CNTs and in S2, the quantity of NiO is rather higher; thus, this sharp fall of transmittance is expected.

The optical band gap of both the samples is calculated using the normal Tauc plot where the intercept of tangent to \((\alpha h\nu)^2\) versus the \(h\nu\) plot with x axis gives the value of optical gap. It is seen that the value of optical gap has increased slightly from 2.51 to 2.75 eV for sample S2.

### 2.4. Thermal Study

Figure 7a,b shows the thermal gravimetric analysis (TGA) and differential thermal analysis (DTA) curve for all three samples, respectively. It is clearly seen that the hybrid sample is much more thermally stable compared with the pure a-CNTs and the stability of the samples increases by increasing the Ni precursor percentage.

Pure a-CNTs show an initial mass loss until 100 °C, which is associated with the evaporation, and then show a steady decrease and at a temperature of 800 °C only 20% of the initial value.

For the hybrid sample, apart from the initial mass loss due to water evaporation, the main weight loss takes place within the temperature range 350–650 °C. At the initial temperature of 350 °C, both the samples have 87% of the initial weight at 650 °C; the S1 sample is degraded to 54% of its initial weight, whereas for S2, the corresponding value is 67% only. The loss is mainly due to desorption of excess oxygen.

From the DTA curves, it is seen that all three samples show an endothermic peak at 50 °C and a broad exothermic peak at 227 °C. The first peak may be associated with the water evaporation, whereas the second one can corresponds to the oxygen desorption. Another broad endothermic peak can be seen around 640 °C but only for S2; for the other two samples, this peak is supposed to be seen at a temperature beyond 800 °C.
The small dissimilarities in the DTA characteristics of pure a-CNT, S1, and S2 are not very surprising since sample S2 has much higher oxide content compared to that of S1 and for pure a-CNTs, it is 0. This effect has been manifested in the DTA characteristics.

2.5. Electrochemical Study. The cyclic voltammetric (C−V) curves for the two hybrid samples have been shown in Figure 8a,b, whereas the same for pure a-CNTs and all related results are shown in our previous work. The specific capacitance \( C_{sp} \) of the hybrids was calculated from the C−V curves using the relation:

\[
C_{sp} = \frac{\int I(V) \, dV}{m(V_c - V_d)}
\]

where \( C_{sp} \) is the specific capacitance (F/g), \( I \) is the current (A), \( m \) is the mass of the electrode active material (g), and \( y \) is the scan rate.
rate (V/s) of C–V curves, and \((V_a - V_c)\) is the potential window (V) for different scan rates.

Figure 9 shows the variation of \(C_{sp}\) with scan rate for both the samples, and it has been shown that the value decreases with increasing scan rates and the value of capacitance reaches around 120 F/g for sample S2 at the lowest scan rate, almost double that of S1. The enhancement is almost 2 orders compared with pure a-CNTs reported in our previous work \(^{21}\) that had a value of around 9 F/g only.

The variation of specific capacitance with the scan rate is rather common, as reported by other workers, and has been explained in terms of speed of the ion movement, mainly insertion and release of Na\(^+\) ion into and from electrode materials and entry into electrolyte solution. \(^{33}\)

The material used here is porous in nature, and thus movement of the ions within the pores would facilitate the electrochemical performance of the material. At a low scan rate, the ions have enough time to reach all of the interior part of the electrodes and thus the amount of charge accumulation is higher, giving a high value of specific capacitance. On the other hand, when the scan rate is high, the cycle change takes place too quickly so that the ions do not have enough time to access the interior part of the porous material and can reach the outer part of the electrodes in general, resulting in a low value of capacitance. \(^{34}\)

Figure 9 shows the variation of specific capacitance value obtained from C–V characteristics with scan rates for both the hybrid samples.

The specific capacitance from C–D curves was calculated using the relation

\[
C_{sp} = \frac{\Delta t \times I}{m \times \Delta E} \tag{2}
\]

where \(I\) is the discharge current (A), \(\Delta E\) is the potential window (V), \(t\) is the discharge time (s), and \(m\) is the mass of the active material (g).

It is seen that again, the capacitance value of the hybrid sample S2 is much higher compared to that of S1, as well as that of pure a-CNTs.

It is worth mentioning that the C–D curves of sample S2 unlike S1 show a flat plateau region for all current densities. The reason for the appearance of such regions is yet to be discovered. However there are a large number of reports that show such regions including the author’s own previous work. \(^{21}\)

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\]

Figure 10a,b shows the typical galvanostatic charge and discharge (C–D) curve of both the hybrid samples for three different current densities, with corresponding variations of specific capacitance shown in Figure 11.

The specific capacitance from charge–discharge characteristics with current density for both hybrid samples.

\[
C_{sp} = \frac{\Delta t \times I}{m \times \Delta E} \tag{2}
\]

where \(I\) is the discharge current (A), \(\Delta E\) is the potential window (V), \(t\) is the discharge time (s), and \(m\) is the mass of the active material (g).

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\]

Figure 10. Charging–discharging characteristics of (a) sample S1 and (b) sample S2 with different current densities.
The value of specific capacitance at highest current density

\[
R = \frac{\text{value of specific capacitance at highest current density}}{\text{value of specific capacitance at lowest current density}} \times 100
\]  

and it has come out to be 35 and 105% for the samples S1 and S2, respectively. Thus, it is seen that with the increase of NiO content, the performance of the sample remains almost the same for different current densities, suggesting favorable use of the hybrids in electrochemical applications.

Other two very important parameters that are related to the electrochemical performance of any material are the energy density \((E)\) and power density \((P)\) obtained from the following relations

\[
E (\text{Wh/kg}) = \frac{1}{2} \times C_{sp} \times V^2
\]

and

\[
P (\text{W/kg}) = E \times \frac{3600}{t}
\]

where \(V\) is the potential window (V) and \(t\) the discharge time (s). The associated parameters calculated from the above formula for both samples and for all current densities are summarized in Table 1, which shows that the hybrid may be used as an efficient electrode material.

The Coulombic efficiency of the sample S2 has been shown in Figure 12, which shows that the efficiency drops down to 93% within few cycles; then, it remains constant up to 10 000 cycles, showing that the material is suitable for long-term operation.

![Figure 12. Coulombic efficiency of the hybrid sample S2 and inset showing energy density of both the samples S1 and S2.](image)

The Nyquist plots of both the hybrid samples are shown in Figure 13 with that of pure a-CNTs shown from our previous work. The plot at the low-impedance region has been shown separately in the inset. It is seen that when the entire region is considered, the plot of S2 consists of three semicircles with a much lower radius of curvature compared to that of S1 that has two semicircles. The results indicate that a-CNTs as well as sample S1 have large charge-transfer resistance \((R_{ct})\), thus hindering transport of charge. On the contrary, a small radius of curvature in the Nyquist plot of sample S2 indicates high conducting nature.

It should be noted that the straight line nature of the imaginary part of the impedance spectra of the Nyquist plot shows the ideal capacitive behavior of the sample.

For NiO-coated a-CNTs, the carbon part prevents the system from degradation due to any mechanical perturbation and thus makes it suitable for long-term stability. Thus, it acts as a structural buffer between the electrodes and electrolytes.

Also, being the transition metal, nickel shows variable valence states and thus it becomes easier for the redox reaction to occur between variable valence states, which helps the system to store energy. The high dielectric constant of the attached NiO, the specific capacitance from the \(C-V\), as well as \(C-D\) curve, has been increased to a great extent.

Table 2 summarizes the electrochemical performance of some carbon and related hybrid-based electrode materials reported recently. It has been seen that this work reports so far the best percentage of increase of capacitance value of the base material in its hybrid form. Also, with respect to the absolute value of capacitance, the material is comparable and sometimes even better compared with the other reported results, with further advantages of an easy, cost effective, and high-yield synthesis procedure.

It is to be noted that other a-CNT-related hybrids show significant enhancement after being hybridized with other oxides or polymer materials of which a-CNT–MnO\(_2\)–polymer composite shows the highest enhancement, whereas a-CNTs–CuO shows the least. a-CNT–MnO\(_2\) hybrid gives comparable

![Figure 13. Nyquist plots of both samples S1 and S2.](image)
results with that of the present work, as expected. It is noteworthy that the research related to amorphous carbon nanotubes has just begun. Thus, the material is now at a stage of being standardized for the best performance. Efforts are being put in studying the capacitor characterization of the material after being functionalized with other materials. Thus, the best performance from this material is yet to be reported for the best hybridization combination.

It is to be noted that the betterment of electrochemical performance of the a-CNT–NiO system takes place due to the proper attachment of the NiO nanostructures on to the a-CNTs’ wall. The attachment is possible without a-CNTs’ being functionalized externally due to their rough wall as well as presence of large numbers of defects of a-CNTs for their being amorphous. Thus, because of this, reported hybrids of a-CNTs being not much active in capacitive behavior hold the system intact for long cycle operation, whereas the oxide part on the wall of a-CNT acted as a capacitive material for obtaining high specific capacitance value and high energy density.

3. CONCLUSIONS

A facile synthesis route for developing a-CNT–NiO nanoflower hybrid electrode has been reported. The microstructures of the as-prepared hybrids were characterized by FESEM and TEM analysis, confirming the successful attachment of NiO nanostructures onto a-CNTs. XRD confirms the amorphousness of the a-CNTs as well as proper phase formation for the NiO nanostructures. Raman as well as FTIR studies indicate the different bonds present in the samples, whereas TGA analysis confirms the thermal stability monotonically increases with increase in NiO amount in the hybrids. As-developed hybrids show efficient electrochemical performance with long-term stability. The specific capacitance obtained from the C–V characteristics has a value, as high as 120 F/g, comparable or better compared with the other reported results, and also, it gives the highest percentage of increment 123% compared to that of pure a-CNTs. The hybrid thus shows long cycle stability and high power density and Coulombic efficiency and also reversible charge–discharge phenomena, thus being suitable for use in highly efficient supercapacitor devices.

4. EXPERIMENTAL SECTION AND CHARACTERIZATION

The synthesis of a-CNTs has been reported in many of our previous works.21 Briefly speaking, a certain amount of ferrocene and a-CNTs were mixed in a 1:2 ratio and thoroughly mixed in a mortar, followed by open atmosphere heating at 225 °C for 30 min. The mixture was then naturally cooled and thoroughly washed with diluted HCl and deionized water. The mixture was then filtered, and the residue was taken and dried in an oven overnight at 60 °C to get the final product.

For preparation of NiO nanostructures, following steps were followed:

The precursors used were, nickel sulfate, potassium persulfate, aqueous ammonia, and ultrapure deionized water. All materials were purchased and used without further purification.

In a typical experiment for two different samples, 0.75 g of potassium per sulfate was added to 1 and 2 g of nickel sulfate separately taken into a beaker filled with 200 mL of deionized water. The mixture was then stirred rigorously to form homogeneous solution. The step was followed by addition of 2.5 mL of aqueous ammonia (25–28%) into the above solution and mixed in a magnetic stirrer for 1 h. The mixture was then filtered, and the residue was dried at 220 °C for 1.5 h. However, the final product was obtained only after annealing it at 300 °C in air for 1.5 h.

Two samples were prepared apart from the pure a-CNTs. In one sample, 0.075 g of a-CNTs were added during stirring with aqueous ammonia, where 1 g of nickel sulfate was added (sample S1) and for the other, 2 g of nickel sulfate was used (sample S2).

The as-prepared pure and hybrid samples were characterized by X-ray diffraction (XRD, Bruker D8 ADVANCE), field emission scanning electron microscopy (FESEM, JEOL 6340F FEG-SEM), high-resolution transmission electron microscopy (HRTEM, JEOL-JEM 2100), a Fourier-transformed infrared

| s.no. | system                          | value of capacitance (F/g) | percentage of increment | reference  |
|-------|---------------------------------|-----------------------------|-------------------------|------------|
|       |                                 | pure system                 | hybrid system           |            |
| 1     | Ni–Co-graphene oxide            | 500 (approx.)               | 1700 (approx.)          | 240        | 16         |
| 2     | functionalized graphene-NiO     | 300 (approx.)               | 400 (approx.)          | 33         | 37         |
| 3     | nitrogen-functionalized CNT     | 42                          | 146                     | 247        | 38         |
| 4     | PEDOT–PSS/CNT                   | 50 (approx.)                | 130 (approx.)          | 106        | 39         |
| 5     | CNT–RuO2                        | 60                          | 138                     | 130        | 40         |
| 6     | MnO2–CNTs                       | 384                         | 482                     | 25         | 41         |
| 7     | CNT–MnO2                        | negligible                  | 467                     |            | 42         |
| 8     | CNT–PPy                         | 230                         | 265                     | 15         | 43         |
| 9     | CNT–PANI                        | 314                         | 403                     | 28         | 44         |
| 10    | MnO2/Mn/MnO2 sandwich-structured| 320 (approx.)               | 937                     | 192        | 45         |
| 11    | ZnO nanorod/amorphous and nanoporous NiO | 198           | 305                     | 54         | 46         |
| 12    | carbon/MnO2 double-walled nanotube | 320 (approx.) | 797                     | 149        | 47         |
| 13    | three-dimensional porous CNT/MnO2 | not given                  | 160.5                   |            | 48         |
| 14    | CNT/MnO2 composites             | 124.9                       | 201                     | 60.8       | 49         |
| 15    | three-dimensional α-Fe2O3/CNT sponge | not given   | 300                     |            | 50         |
| 16    | CNT–NiO nanosheets              | 288                         | 996                     | 245        | 51         |
| 17    | a-CNT–CuO                       | 9                           | 47.6                    | 428        | 20         |
| 18    | a-CNT–MnO2–PPy                  | 9                           | 200                     | 2100       | 21         |
| 19    | a-CNT–MnO2                      | 9                           | 145                     | 1500       | 22         |
| 20    | a-CNT–NiO                       | 9                           | 120                     | 1230       | present work |
spectrometer (Shimadzu FTIR-8400S), a Raman spectrometer (Witec, $\lambda_{\text{excitation}} = 532$ nm), a UV-vis spectrophotometer (JASCO V-750), and TG-DTA analysis (TG-DTA, PerkinElmer). The detailed electrochemical characterization was done using a PHE200 Physical Electrochemistry Software with a Gamry’s Potentiostat with 1 M Na$_2$SO$_4$ electrolyte solution at room temperature. The amounts of working samples (S1 and S2) taken for electrode preparation were 0.8 gm.

The sample preparation for the electrochemical measurement was as follows:

All measurements were done with a three-electrode system, where the reference electrode of Ag/AgCl and a counter electrode of platinum were used. The working electrodes were developed by the same process described in our previous work.$^2$

The electrochemical performance was studied both from cyclic voltammetry study as well as galvanostatic charging-discharging study. Five different scan rates, like 10, 20, 50, 100, and 200 mV/s, were employed within 0—1 V range to study the C–V characteristics. Electrochemical impedance spectroscopy was operated between frequency ranges of 0.01—10$^5$ Hz at 0.5 V with an alternating current voltage amplitude of 50 mV.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors wish to acknowledge the Department of Science and Technology (DST; SERB; Gov’t of India) (SR/FTP/ETA-408/2013) for the financial support during the execution of the work.

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