Cellulose Nanocrystal Templated Graphene Nanoscrolls for High Performance Supercapacitors and Hydrogen Storage: An Experimental and Molecular Simulation Study

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Graphene nanoscrolls (GNS), due to their remarkably interesting properties, have attracted significant interest with applications in various engineering sectors. However, uncontrolled morphologies, poor yield and low quality GNS produced through traditional routes are major challenges associated. We demonstrate sustainable approach of utilizing bio-derived cellulose nanocrystals (CNCs) as template for fabrication of GNS with tunable morphological dimensions ranging from micron-to-nanoscale (controlled length < 1 μm or > 1 μm), along with encapsulation of catalytically active metallic species in scroll interlayers. The surface-modified magnetic CNCs acts as structural-directing agents which provides enough momentum to initiate self-scrolling phenomenon of graphene through van der Waals forces and π-π interactions, mechanism of which is demonstrated through experimental and molecular simulation studies. The proposed approach of GNS fabrication provides flexibility to tune physico-chemical properties of GNS by simply varying interlayer spacing, scrolling density and fraction of encapsulated metallic nanoparticles. The hybrid GNS with confined palladium or platinum nanoparticles (at lower loading ~1 wt.%) shows enhanced hydrogen storage capacity (~0.2 wt. % at ~20 bar and ~273 K) and excellent supercapacitance behavior (~223–357 F/g) for prolonged cycles (retention ~93.5–96.4% at ~10000 cycles). The current strategy of utilizing bio-based templates can be further extended to incorporate complex architectures or nanomaterials in GNS core or inter-layers, which will potentially broaden its applications in fabrication of high-performance devices.

Graphene nanoscrolls (GNS) are one of the most emerging carbon-based nanomaterials which have been the focus of several recent studies due to their interesting physico-chemical properties and one-dimensional topological structures produced through rolling of two-dimensional graphene sheets. GNS are morphologically similar to multiwalled carbon nanotubes (CNTs); however, their open end structures, variable scrolling density and tunable inter-layer spacing provides a unique opportunity to inherit favorable properties of both CNTs and graphene. The tubular nanochannels and high porosity present in GNS provides pathway for intercalation of ionic species in its inter-galleries resulting in higher electrical conductivities compared to graphene with practical applications in electrochemical charge storage devices and electronics. In literature, molecular simulation-based studies on the formation of GNS and theoretical predictions of its properties, have been extensively studied. However, self-assembly of GNS through real-time experiments is technically difficult to achieve. Despite the unique properties of GNS, it has been shown to undergo unwrapping leading to formation of defects, due to which studies on potential applications of GNS in hydrogen (H2) storage devices, CO2 capture and catalysis have been only possible through simulation studies. Some of the investigations for fabrication of GNS are based on self-assembly of graphene through controlled sonication approaches, Langmuir-Blodgett, cyclic freezing-thawing, chemical
Fabrication of graphene nanoscrolls (GNS) using Fe$_2$O$_3$-CNC as templates: Effect of CNC aspect ratio. The surface modified magneto-responsive CNCs acts as a template for scrolling of graphene sheets to form GNS with tunable morphology and inter-layers, which depends upon the aspect ratio of initial substrate. In this study, after exfoliation, the graphene sheets were sonicated for a fixed duration of time (~30 mins in methanol) which leads to the formation of size-specific GRO sheets with dimensional area of 0.56±0.3 µm$^2$ (as shown in Fig. S1(a and b)). The FESEM micrographs and collected TEM micrographs shows the presence of several bunches of the GRO sheets, which further confirms its similar morphological dimensions. The fabricated Fe$_2$O$_3$-CNCs (as discussed in Supporting Information, Part I) have high fractions (~35 wt%) of maghemite nanoparticles decorated on its surface, which integrates magnetic moment of ~43 emu/g alongwith the distinct rod-like morphology (length ~745 ± 63 nm and diameter ~56 ± 8 nm), makes it an ideal candidate for GNS fabrication (Fig. S2(a-g)). It is noteworthy to state that due to polydisperse nature of CNCs and graphene sheets, it is difficult to control the dimensions of GNS, however, the main objective of this study is to fabricate GNS with length in range of micron and nanoscale dimensions (with controlled length < 1µm or >1µm), from the application point of view (as discussed in Introduction). FESEM and TEM micrographs shows bunch of GNS (Fig. 1(a,b and c)) fabricated using low aspect ratio Fe$_2$O$_3$-CNCs as templates (Fe$_2$O$_3$-NS-LR), with length ~750 ± 230 nm and diameter ~174 ± 50 nm. Interestingly, it was observed that dimensions of fabricated Fe$_2$O$_3$-NS especially its length is found to be almost similar to that of Fe$_2$O$_3$-CNCs (which is further confirmed from the collected TEM micrographs, Fig. S4(a)). However, the increased diameter is probably due to adherence of multiple epoxidized Fe$_2$O$_3$-CNCs onto graphene sheets during the GNS formation process. High resolution FESEM micrographs (Fig. 1(b and b')) of individual Fe$_2$O$_3$-NS shows the presence of Fe$_2$O$_3$ nanoparticles confined in its core with end tip showing the scrolling of graphene sheets with open ends. The investigations of HR-TEM micrographs of Fe$_2$O$_3$-NS edge shows the presence of multiple-layers of graphene sheets (marked with black arrows) with intercalated Fe$_2$O$_3$ nanoparticles in its core as well as inter-layers (marked with white arrows, Fig. 1(f)). Further, EDX mapped image of selected Fe$_2$O$_3$-NS shows the presence of Fe$_2$O$_3$ nanoparticles with a composition of ~6.2 wt.% Fe (Fig. 1(e and g)). Therefore, from morphological and elemental analysis it could be confirmed that Fe$_2$O$_3$-CNCs acts as structural directing agent which provides enough momentum to initiate scrolling of graphene sheets to form Fe$_2$O$_3$-NS with encapsulated Fe$_2$O$_3$ nanoparticles.

To further investigate the effect of CNC dimensions on GNS formation, high aspect ratio precursor Fe$_2$O$_3$-CNC-HR is formed using the CNCs derived from filter paper$^{19}$ (as detailed in Supporting Information, Part I). Utilization of Fe$_2$O$_3$-CNC-HR (with length ~2.8 ± 0.8 µm and diameter ~82 ± 18 nm) (Fig. S3) as template, lead to the formation of Fe$_2$O$_3$-NS with length ~4.5 ± 1.2 µm and diameter ~0.37 ± 0.21 µm as evident from FESEM and TEM micrographs (Fig. 2(a and d)), respectively. It could be observed that the fabricated Fe$_2$O$_3$-NS-HR are in micron dimensions (with length >1µm) which have successfully inherited the
Figure 1. (a) FESEM images of the Fe₂O₃-NS fabricated using low aspect ratio Fe₂O₃-CNCs as initial precursor, (b) and (b') High resolution FESEM micrographs of a Fe₂O₃-NS (at magnification ~230KX) shows the presence of the Fe₂O₃ nanoparticles in its core and scrolling of the graphene sheets to form an open end GNS, (c) and (d) TEM micrographs of the low aspect ratio Fe₂O₃-NS, (e) and (e') shows the EDX map of the selected region in the FESEM micrographs for a Fe₂O₃-NS encapsulated with Fe₂O₃ nanoparticles (f) TEM image of an edge of Fe₂O₃-NS which shows number of graphene layers (marked with black arrows) and the encapsulated Fe₂O₃ nanoparticles (marked with white arrows) and (g) compositional analysis of the Fe₂O₃-NS.

structural properties of Fe₂O₃-CNC-HR (as also confirmed through the collected FESEM micrographs shown in Fig. S4(b)). Further, Fe₂O₃-NS shows the presence of the open ends suggesting its hollow nature (Fig. 2(b)) which have thin layer of graphene sheets wrapped on Fe₂O₃ nanoparticles (Fig. 2(c and d')). The compositional
analysis of Fe₂O₃-NS-HR contains ~15 wt% of Fe₂O₃ nanoparticles (Fig. 2(e)) which is higher in comparison to Fe₂O₃-NS-LR due to adsorption of higher fragments of Fe₂O₃-CNCs onto graphene sheets during GNS formation. Similarly, HRTEM micrographs in case of Fe₂O₃-NS-HR (Fig. 2(f)) shows presence of higher number of multi-layered graphene sheets rolled on it compared to Fe₂O₃-NS-LR. This is probably due to high fractions of Fe₂O₃ nanoparticles in the inner cores of Fe₂O₃-NS-HR which results in higher magnetic moment, providing enough torque on graphene sheets to overcome the threshold energy barrier and undergo scrolling phenomenon to form multi-layered structure onto Fe₂O₃-CNCs. Similar theoretical observations was also reported by Wang et al. (2015) on utilization of low aspect ratio carbon nanotubes as structural directing agent which failed to initiate the nanoscroll formation process, due to its lowered van der Waals interaction energy. Figure 2(g), shows the lattice fringes with interlayer spacing of ~0.35 nm represents (200) crystal planes of graphene sheets, confirming its presence. Therefore, it could be inferred that both morphology and density of scrolled graphene in Fe₂O₃-NS can be remotely controlled by simply tuning the density of maghemite nanoparticles as well as magnetic moment/
resents (400) and (440) planes of Fe$_2$O$_3$ nanoparticles, respectively. The low intensity XRD peaks of Fe$_2$O$_3$ in (311), (400), (422), (511) and (440) planes of Fe$_2$O$_3$ nanoparticles respectively, which confirms their presence of the Fe$_2$O$_3$-NS. From the electron diffraction pattern, presence of the concentric hexagons represents the pack-visualized from which the profile of the intensities was calculated to determine the structure and lattice parameter considering the equatorial line of the SAED pattern. On the marked equatorial line, four spots can be distinguisly from the FTIR and Raman spectroscopy studies. As reported in our earlier studies, the abundant hydroxyl groups in CNCs provides sites for the precipitation of Fe$_2$O$_3$ nanoparticles on its surface, which was confirmed from the presence of peak at ~620 cm$^{-1}$ and shoulder peak at ~700 cm$^{-1}$ corresponding to Fe-O vibrations, absence of the free hydroxyl peaks of CNC at 3280 cm$^{-1}$ and shift of peak (-OH stretching) at ~1646 cm$^{-1}$ (in CNCs) to 1652 cm$^{-1}$ (Fig. S5(a)). Further, on modifications epoxidized Fe$_2$O$_3$-CNCs shows the presence of new peaks at ~3434 cm$^{-1}$ corresponding to the C-H stretching vibration of epoxy groups in epichlorohydrin and with formation of small peak at ~1290 cm$^{-1}$ (C-O-C stretching) confirms the presence of epoxidized ring in modified Fe$_2$O$_3$-CNCs. The FTIR spectrograph of the GRO sheets (after sonication in presence of the hydrogen peroxide) shows the presence of peaks at 3550 cm$^{-1}$, 1200 cm$^{-1}$, 1070 cm$^{-1}$ and 1720 cm$^{-1}$ corresponding to O-H stretching, C-O epoxy stretching, C-O alkoxy stretching and C=O carbonyl stretching vibrations respectively. In Fe$_2$O$_3$-CNC-NS, the new peaks at ~3504 cm$^{-1}$ corresponds to -OH stretching and 1595 cm$^{-1}$ denotes skeletal vibrations from graphitic rings of GRO sheets along with the decrease in intensity of peaks at 1062 cm$^{-1}$, 1114 cm$^{-1}$ and 1158 cm$^{-1}$ (rep-representing -C-O-C asymmetric stretching of β-glucosidic linkage, C-OH stretching in plane at C-6, and -C-O-C dimensions of Fe$_2$O$_3$-CNCs (template), which provides a facile approach of fabricating GNS with tunable properties depending upon the targeted applications.

Figure 3(a) shows XRD diffractograms of Fe$_2$O$_3$-NS formed with different aspect ratio which shows presence of peak at 20 = 26.5° corresponding to graphene representing (002) planes$^{11}$. The XRD spectra for Fe$_2$O$_3$-NS-HR, shows the presence of distinctive peaks at 20 = 30.4°, 35.6°, 43.2°, 54.5°, 57.3° and 63.1° corresponding to (220), (311), (400), (422), (511) and (440) planes of Fe$_2$O$_3$ nanoparticles$^{20}$ respectively, which confirms their presence in core of GNS. However, in case of Fe$_2$O$_3$-NS-LR, presence of small intensity peaks at 20 = 43.2° and 62.5° represents (400) and (440) planes of Fe$_2$O$_3$ nanoparticles, respectively. The low intensity XRD peaks of Fe$_2$O$_3$ in case of Fe$_2$O$_3$-NS-LR, is probably due to presence of low fractions of Fe$_2$O$_3$ nanoparticles alongwith presence of graphene layers covering its surface. Therefore, XRD diffractograms of both high and low aspect ratio GNS confirms presence of Fe$_2$O$_3$ nanoparticles in scrolled graphene sheets. The SAED pattern of Fe$_2$O$_3$-NS interestingly shows the presence of sharp hexagonal spots which are concentric in nature with the presence of equatorial line showing that the diffraction pattern of GNS consists of intense spots along a line perpendicular to the needle axis. The presence of the multiple and concentric diffraction patterns (marked with dotted white lines) suggests that graphene sheets have undergone scrolling phenomenon to form a multilayered rolled structure, which arises due to the diffractions from the individual set of rolled graphene sheets$^{11}$ present in the Fe$_2$O$_3$-NS. The presence of the equatorial line along the spots [0004] and [002]$^{22}$, suggest that the presence of the parallel graphene layers with stacking periodicity (and perpendicular orientation with respect to electron beam) which confirms the formation of Archimedean spiral in the inner core of the Fe$_2$O$_3$-NS. Figure S5(b), shows the SAED pattern of the Fe$_2$O$_3$-NS which shows the presence of the well-defined diffraction spots with an ordered continuity along the equatorial line. Information on the degree of packing of the multi-layered GRO sheets in the Fe$_2$O$_3$-NS can be obtained by considering the equatorial line of the SAED pattern. On the marked equatorial line, four spots can be distinguisly visualized from which the profile of the intensities was calculated to determine the structure and lattice parameter of the Fe$_2$O$_3$-NS. From the electron diffraction pattern, presence of the concentric hexagons represents the pack-ing of the multi-layered graphene sheets which have occurred during the scrolling of the GRO sheets. Further, in line with the previously reported literature it was observed that the equatorial line rotates along the centre of polygon with the presence of high intensity spots present at its curves (towards radial directions), suggesting, the circular morphology of the Fe$_2$O$_3$-NS (present at its cross-section). Evaluation of the SAED pattern and the intensity profiles (Fig. S5(b and c)) of the selected section of Fig. S5(a), suggests the presence of two bundles of Fe$_2$O$_3$-NS with interlayer spacing of 0.318 nm.

The epoxidation of Fe$_2$O$_3$-CNCs followed by scrolling of graphene sheets to form Fe$_2$O$_3$-NS, are confirmed from the FTIR and Raman spectroscopy studies. As reported in our earlier studies$^{23}$, the abundant hydroxyl groups in CNCs provides sites for the precipitation of Fe$_2$O$_3$ nanoparticles on its surface, which was confirmed from the presence of peak at ~620 cm$^{-1}$ and shoulder peak at ~700 cm$^{-1}$ corresponding to Fe-O vibrations, absence of the free hydroxyl peaks of CNC at 3280 cm$^{-1}$ and shift of peak (-OH bending) at ~1646 cm$^{-1}$ (in CNCs) to 1652 cm$^{-1}$ (Fig. S5(a)). Further, on modifications epoxidized Fe$_2$O$_3$-CNCs shows the presence of new peaks at ~3434 cm$^{-1}$ corresponding to the C-H stretching vibration of epoxy groups in epichlorohydrin and with formation of small peak at ~1290 cm$^{-1}$ (C-O-C stretching) confirms the presence of epoxidized ring in modified Fe$_2$O$_3$-CNCs. The FTIR spectrograph of the GRO sheets (after sonication in presence of the hydrogen peroxide) shows the presence of peaks at 3550 cm$^{-1}$, 1200 cm$^{-1}$, 1070 cm$^{-1}$ and 1720 cm$^{-1}$ corresponding to O-H stretching, C-O epoxy stretching, C-O alkoxy stretching and C=O carbonyl stretching vibrations respectively. In Fe$_2$O$_3$-CNC-NS, the new peaks at ~3504 cm$^{-1}$ corresponds to -OH stretching and 1595 cm$^{-1}$ denotes skeletal vibrations from graphitic rings of GRO sheets alongwith the decrease in intensity of peaks at 1062 cm$^{-1}$, 1114 cm$^{-1}$ and 1158 cm$^{-1}$ (rep-representing -C-O-C asymmetric stretching of β-glucosidic linkage, C-OH stretching in plane at C-6, and -C-O-C...
asymmetric bending of (β-glucosidic linkage) confirms scrolling of graphene onto Fe\textsubscript{2}O\textsubscript{3}-CNCs by ring opening in epoxidized Fe\textsubscript{2}O\textsubscript{3}-CNC through formation of C-O-C bonding. On calcination of Fe\textsubscript{2}O\textsubscript{3}-CNC-NS, it was observed that the intensity of the various oxygen functionalities suppressed which is possibly due to the reduction of the partially oxidized GRO sheets to graphene\textsuperscript{22}. The Raman spectra of GRO sheets shows a G-band at ~1582 cm\textsuperscript{-1} and D-band at ~1354 cm\textsuperscript{-1} with an I\textsubscript{D}/I\textsubscript{G} ratio of ~0.97 (Fig. 3(b)). The epoxidation of Fe\textsubscript{2}O\textsubscript{3}-CNCs followed by its reaction with partially oxidized GRO (GRO) sheets brings it in close proximity which is a necessary step to initiate the nanoscrolls formation process that occurs through π-π interactions and magnetic manipulation\textsuperscript{25}. Due to such phenomenon, the epoxidized Fe\textsubscript{2}O\textsubscript{3}-CNCs adheres to inner core of GNS through sp\textsuperscript{2}-hybridization, which leads to formation of open-ended GNS with more defects that could be evaluated through values of I\textsubscript{D}/I\textsubscript{G} ratio\textsuperscript{11}. However, it was observed that presence of such scrollering phenomenon was completely absent in presence of the unmodified CNCs as shown in Fig. SS(d), with the presence of bunch of CNCs lying on the surface of GRO sheets (Fig. SS(d')). Therefore, it could be concluded that the Fe\textsubscript{2}O\textsubscript{3}-CNCs are responsible to initiate the scrolling of the graphene sheets resulting in the formation of Fe\textsubscript{2}O\textsubscript{3}-NS. Further, the effect of Fe\textsubscript{2}O\textsubscript{3}-CNCs on morphology of GNS also lead to significant alteration in Raman spectra with increased I\textsubscript{D}/I\textsubscript{G} ratio ~1.03 for Fe\textsubscript{2}O\textsubscript{3}-NS-LR in comparison to Fe\textsubscript{2}O\textsubscript{3}-NS-HR ~1.01. As evident from morphological studies (Figs 1 and 2(f)), lower I\textsubscript{D}/I\textsubscript{G} values for Fe\textsubscript{2}O\textsubscript{3}-NS-HR suggests lower defects that will increase graphene layers in GNS compared to Fe\textsubscript{2}O\textsubscript{3}-NS-LR, which have higher defects along with low scrolling density due to its increased sp\textsuperscript{2}-hybridization. Further form Raman spectroscopy, it could be confirmed that GNS with variable scrolling density and tunable morphological dimensions can be fabricated by simple altering the aspect ratio of CNCs.

**Mechanism for graphene nanoscrolls formation using Fe\textsubscript{2}O\textsubscript{3}-CNCs as templates: Molecular simulation studies.** In order to understand the mechanism and driving forces responsible for formation of GNS onto Fe\textsubscript{2}O\textsubscript{3}-CNCs substrate, molecular simulation studies are carried out which is jointly corroborated with the experimental findings (electron micrographs obtained during optimization of GNS fabrication process) (Fig. 4(a)). As addressed from experimental studies that the effect of aspect ratio of initial substrate Fe\textsubscript{2}O\textsubscript{3}-CNCs and their high magnetic behaviour are responsible for the formation of nanoscrolls is further verified through MD simulation studies. As a typical representation of experimental studies, a molecular model of Fe\textsubscript{2}O\textsubscript{3}-CNC with a low aspect ratio (~13), similar magnetic properties and loading fractions of Fe\textsubscript{2}O\textsubscript{3} nanoparticles (~35 wt%) was prepared followed by its geometry optimization to obtain energy minimized morphology. The Fe\textsubscript{2}O\textsubscript{3}-CNC was placed at the centre of a graphene sheet (with length ~116.2 Å and width ~58.1 Å) along the axis of Fe\textsubscript{2}O\textsubscript{3}-CNC (Fig. 4a(i)). On geometry optimization, Fe\textsubscript{2}O\textsubscript{3}-CNC approaches closer to the surface of graphene sheet because of the presence of favourable attractive forces in between the two moieties. Thereafter, MD study was carried out on the prepared structure over a time period of ~400 ps to observe conformational changes as well as understand the effect of van der Waals (vdW) interaction forces between graphene sheets and Fe\textsubscript{2}O\textsubscript{3}-CNC. The formation and growth mechanism of Fe\textsubscript{2}O\textsubscript{3}-NS can be classified into two steps: firstly the nucleation of Fe\textsubscript{2}O\textsubscript{3}-CNCs onto graphene sheets followed by the second step in which self-scrolling of graphene on its surface to form GNS takes place over a period of time to form tight scrolls (see video S1 in supplementary information). Initially at t = 0 ps, presence of Fe\textsubscript{2}O\textsubscript{3}-CNC results in formation of discontinuous wrinkled structures on the graphene sheets indicating thermodynamic instability until t = 100 ps. It is evident from the total energy and vdW interaction energy plots which shows a slight drop till t = 20 ps due to improved interactions and thereafter remains almost constant till t = 200 ps. Similar observations on wrinkled state of graphene sheets with bunch of Fe\textsubscript{2}O\textsubscript{3}-CNCs adhered on its surface are evident from experimental studies as shown in Fig. 4(a). After time period of t = 200 ps, the initial curl of graphene sheet starts to occur on the Fe\textsubscript{2}O\textsubscript{3}-CNC surface from one side of edge. The initiation of curl of graphene sheet is visible from TEM micrographs (Fig. 4a(ii)) which shows the formation of twisted morphology along the ends of Fe\textsubscript{2}O\textsubscript{3}-CNCs (marked in blue arrow) adhered to the surface of GRO. In next 300 ps, the graphene sheet starts to roll on the surface of Fe\textsubscript{2}O\textsubscript{3}-CNC from one end (left side first) and tries to adjust to obtain the best possible stable configuration (as shown in Fig. 4a(iii and iv)). It is observed that the graphene layers slide over the Fe\textsubscript{2}O\textsubscript{3}-CNC slowly during which the total and potential energy remain almost constant. The intermediate step for partially scrolled graphene sheet layers onto Fe\textsubscript{2}O\textsubscript{3}-CNC surface can be observed from the FESEM micrographs (marked with blue arrow as shown in Fig. 4a(iv and v)). After t = 300 ps, structural transition of the 2D planar structure of graphene takes place to form a 1D tubular GNS due to strong interaction between the graphene sheets and Fe\textsubscript{2}O\textsubscript{3}-CNC. The transition is also evident from the sharp drop in potential as well as total energy values (as shown in Fig. 4(b)) during the time span of ~320–350 ps, which suggest that the system has undergone significant structural alteration to attain a minimum energy state. In this state, the graphene sheet completely covers the surface of Fe\textsubscript{2}O\textsubscript{3}-CNC and acquires the structural configuration of the rod-like morphology of the Fe\textsubscript{2}O\textsubscript{3}-CNC (Fig. 4a(vi and vii)). Due to presence of high loadings of Fe\textsubscript{2}O\textsubscript{3} nanoparticles and its improved interfacial interaction with the graphene sheets undergoes scrolling as visualized from the rolled edges to form a complete nanoscroll morphology. From the molecular simulation studies, it was observed that the energy of the intermediate state of bending for the graphene sheet of length of ~116 Å, was found to be 1021 kcal/mol in this study using the Fe\textsubscript{2}O\textsubscript{3}-CNCs (of aspect ratio ~13 and with incorporated ~35 wt.% of Fe\textsubscript{2}O\textsubscript{3} nanoparticles) as structural directing agents. It is noteworthy to mention that the energy of the intermediate state of bending of the graphene sheets to form GNS will significantly depend upon the morphological, physico-chemical properties and functionalization of the structural directing agents as well as graphene sheets. Eventually, after simulation run of ~400 ps, a complete nanoscroll is formed with the encapsulated Fe\textsubscript{2}O\textsubscript{3}-CNC in its core with dimensions of length similar to the template. Interestingly, the simulated Fe\textsubscript{2}O\textsubscript{3}-NS have slightly larger diameter compared to the template which was also observed in the experimental studies (FESEM/TEM of both Fe\textsubscript{2}O\textsubscript{3}-NS-HR and Fe\textsubscript{2}O\textsubscript{3}-NS-LR) suggesting that the central hollow core of Fe\textsubscript{2}O\textsubscript{3}-NS will be slightly larger than template diameter. In experimental conditions, the CNCs are removed through a controlled calcination process which further helps.
in scrolling of graphene sheets into perfect nanoscrolls mimicking the morphological dimensions of template with confinement of catalytically active metallic nanoparticles in its core.

**Fabrication of graphene nanoscrolls: Encapsulated catalytically active nanoparticles.**

Along with the tunable dimensions of GNS, the main objective of this study is to introduce different types of catalytically active metal precursors in its core which widens application of GNS in various sectors. Pd-Fe₂O₃-CNC and Pt-Fe₂O₃-CNC with high magnetic moment (~26.4 and 19.4 emu/g respectively) (Fig. S6(a–i)) and distinct rod/fiber-like morphology are used as templates for fabrication of GNS (as discussed in Supporting Information, Part II). In earlier reported literature, attempt to incorporate palladium oxide nanoparticles in GNS core didn’t show any rolling behaviour. This is probably due to the absence of magnetic behaviour as well as structural directing templates which prevents graphene sheets to overcome the threshold energy required to initiate scrolling phenomenon. It has been observed through simulation studies that the separation distance between graphene and adsorbed nanoparticles is a key factor in initiating the scrolling process which is governed by vdW force of interaction. During covalent functionalization of Pt/Pd-Fe₂O₃-CNC with graphene sheets through epoxidation process is expected to bring the two materials in close proximity which helps in overcoming the energy
crystal of Fe$_2$O$_3$ nanoparticles and low intensity peaks at $\theta \approx 26.6^\circ$. TEM micrographs show uniformly distributed monodisperse Pd nanoparticles (in size range of $10 \pm 2$ nm) along the length of nanoscrolls (marked with white arrows) with the presence of multiple-layered graphene scrolled (marked in black arrows) which have confined Pd nanoparticles in its core as well as inter-galleries. Interestingly, HRTEM micrographs (Fig. 5(f)) shows the presence of cross-over lattice fringes of $0.350$ and $0.200$ nm corresponding to $(200)$ and $(111)$ crystal planes for graphene and Pd nanoparticles respectively. Further, line EDX spectra confirms the presence of both Pd and Fe elements with composition of $\sim 1.8$ wt.$\%$ and $\sim 0.7$ wt.$\%$ respectively, which suggests that utilization of magneto-responsive CNCs developed in this study acts as an unique template for introduction of catalytically active mofeties in core of GNS.

To evaluate the robustness of Fe$_2$O$_3$-CNCs as structural directing agents for GNS formation, this study was further extended to encapsulate other forms of catalytically active Pt nanoparticles at lower loading fractions and evaluate the changes in its physico-chemical properties. Morphological analysis shows Pt-Fe$_2$O$_3$-NS are of length $\sim 810 \pm 90$ nm and diameter $\sim 95 \pm 20$ nm respectively, which is comparable with length of Fe$_2$O$_3$-NS with slight decrease in the diameter (Fig. 6(a–c)). It is expected that shrinkage in diameter of Pd/Fe$_2$O$_3$-NS might occur during calcination process when CNCs are removed from GNS core leaving behind Fe$_2$O$_3$/Pt-Pd nanoparticles while self-scrolling of graphene sheets due to inter-particle van der Waals force of attraction resulting in reduction of diameter. TEM micrographs displays bunch of hollow Pt-Fe$_2$O$_3$-NS with open ends and intercalated Pt nanoparticles (in size range of $11 \pm 1$ nm) distributed on its surface with thin layer of graphene sheets rolled on it (Fig. 6(d,e)), as confirmed from lattice spacing of $\sim 0.35$ nm representing $(200)$ plane of graphene (Fig. 6(f)). Further, EDX-map of Pt-Fe$_2$O$_3$-NS shows uniform distribution of Pt nanoparticles with composition of $\sim 1.6$ wt.$\%$ confined in its core. Therefore, through strategic modifications of CNCs various types of catalytically active metallic nanoparticles can be confined in core of GNS with controlled loading fractions depending upon the desired catalytic activity required for targeted applications.

XRD diffractograms of Pd-Fe$_2$O$_3$-NS and Pt-Fe$_2$O$_3$-NS (Fig. 6(h)) shows broadening of peak at $2\theta = 26.6^\circ$ (corresponds to $(002)$ planes of graphene) compared to sharp peak for GRO. Further, for Pd-Fe$_2$O$_3$-NS peak at $2\theta = 26.6^\circ$ shifts to $25.5^\circ$ which is possibly due to scrolling of graphene sheets with different size of intercalated Pd/ Pt nanoparticles. Such alteration of diffraction peak of GNS(002) was also observed by Xu et al. on intercalation of different solvents followed by its swelling and drying. Pd-Fe$_2$O$_3$-NS shows peaks at $2\theta = 40.0^\circ$, $46.5^\circ$ and $67.8^\circ$ representing $(111)$, $(200)$ and $(220)$ crystal planes of Pd nanoparticles$^{24}$, peaks at $2\theta = 35.5^\circ$ corresponds to $(311)$ crystal of Fe$_2$O$_3$ nanoparticles and low intensity peaks at $2\theta = 38.6^\circ$ and $53.4^\circ$ designates $(311)$ and $(422)$ crystal planes of Fe$_2$O$_3$ nanoparticles. Similarly, Pt-Fe$_2$O$_3$-NS shows peaks at $2\theta = 39.9^\circ$, $46.3^\circ$ and $67.9^\circ$ representing $(111)$, $(200)$ and $(220)$ crystal planes of Pt nanoparticles$^{25}$, peaks at $2\theta = 35.6^\circ$ corresponds to $(311)$ crystal of Fe$_2$O$_3$ nanoparticles and a small peak at $2\theta = 38.6^\circ$ designates $(311)$ crystal planes of Fe$_2$O$_3$ nanoparticles. The absence of any peak corresponding to CNCs crystallites suggests its complete removal, however, diffractograms shows presence of small intensity peaks of Fe$_2$O$_3$ nanoparticles which have plausibly formed during calcination process. Investigations of crystallites sizes of Pd/Pt nanoparticles (using Scherrer’s equation) encapsulated within GNS are $\sim 8.6$ nm and $10.7$ nm respectively which comparatively matches with dimensions measured from TEM micrographs. This suggests that Pd/Pt nanoparticles adsorbed on CNCs can be effectively transferred to inner core of GNS without any significant agglomeration or accumulations of nanoparticles. From comparison of Raman spectra it was observed that $I_D/I_G$ ratio for GRO $\approx 0.97$, which increased to $\sim 1.01$ and $1.03$ for Pd and Pt-Fe$_2$O$_3$-NS respectively (Fig. 6(i)). The increased $I_D/I_G$ ratio is attributed to formation of new defects as well as sp$^3$ hybridization which might have occurred during epoxidation of graphene sheets with Pd/Fe$_2$O$_3$-CNC as well as calcination of CNCs to form hollow core. Moreover, increased broadness and intensity of G band in case of Pd/Fe$_2$O$_3$-NS is probably due to scrolling up of graphene sheets into multilayers which increases elastic strain on it. From crystallographic and spectroscopic studies, it was observed that the proposed methodology for fabrication of GNS efficiently utilizes CNCs as templates for encapsulation of wide variety of metallic nanoparticles inside GNS core depending upon targeted applications.

**Graphene nanoscrolls for hydrogen adsorption studies.** The fabricated GNS have nanoscale hollow cylindrical channels doped with transition metal precursors such as Pd and Pt nanoparticles which is expected to provide a favourable route for hydrogen (H$_2$) transport and storage. The H$_2$ uptake for Pt-Fe$_2$O$_3$-NS and Pd-Fe$_2$O$_3$-NS are found to be $\sim 0.17$ and $\sim 0.14$ wt.$\%$ respectively (measured at 273 K and 20 bar) which is improved by $\sim 112\%$ in comparison to GRO (Fig. 7(a)). Most of the studies reported in literature on H$_2$ adsorption of CNCs are based on MD simulations, with a recent study showing H$_2$ uptake of $\sim 7$ wt.$\%$ at 77 K, 25 bar and $\sim 0.4$ wt.$\%$ at 273 K, 25 bar pressure$^8$, which is comparable to our experimental results. Interestingly, even with very low surface area of Pt-Fe$_2$O$_3$-NS and Pd-Fe$_2$O$_3$-NS ($20.5$ and $21.3$ m$^2$g$^{-1}$ respectively) and lower fractions of encapsulated Pt/Pd nanoparticles ($\sim 1$ wt.$\%$), significant improvement in H$_2$ capacity is observed. This is probably due to the presence of encapsulated Pt/Pd nanoparticles which could dissociate H$_2$ into H atoms through spill over mechanism$^{26}$ followed by its entrapment in the GNS nanochannels through physio or chemisorption with unsaturated graphene layers (detailed mechanism explained in Fig. 7(b)). Therefore, it could be concluded that GNS with confinement of Pd/Pt nanoparticles (even at lower loadings) through the utilization of biobased nanomaterial as template, provides a novel approach to develop H$_2$ storage devices operational at relatively feasible conditions (low pressure $\sim 20$ bar and 273 K).

**Electrochemical performance of graphene nanoscrolls as supercapacitors.** The scrolled topology of GNS favours the formation of electric double layer capacitors (EDLCs) alongwith the encapsulated metallic
Figure 5. (a) FESEM micrographs of the fabricated Pd-Fe$_2$O$_3$-NS (with the inset showing a single GNS with the encapsulated Pd nanoparticle in its centre), (b) Pd-Fe$_2$O$_3$-NS FESEM micrograph at higher resolution, (c) and (d) TEM micrographs of the Pd-Fe$_2$O$_3$-NS with the encapsulated Pd nanoparticles in it (marked with white arrows) (c') Inset displays the magnified open end of the Pd-Fe$_2$O$_3$-NS (marked with rectangular box), (e) TEM micrograph of a edge of Pd-Fe$_2$O$_3$-NS which shows the presence of multiple layer of graphene sheets rolled (marked with black arrows) with the Pd nanoparticles (marked in white arrows) encapsulated in its core and surface. (f) HRTEM micrographs of Pd-Fe$_2$O$_3$-NS illustrating the presence of lattice fringes of Pd nanoparticles and graphene, (g) and (h) FESEM-EDX line-spectra of the selected region (marked in black line) showing the distribution of the Pd and Fe elements on the Pd-Fe$_2$O$_3$-NS and (i) compositional analysis of the elements in the Pd-Fe$_2$O$_3$-NS.
Figure 6. (a) FESEM micrographs of the fabricated Pt-Fe₂O₃-NS (marked with black arrows), (b) FESEM micrograph at higher resolution (with the inset showing a single GNS with the encapsulated Pt nanoparticle in its centre), (c) and (d) TEM micrographs of the Pt-Fe₂O₃-NS with the encapsulated Pt nanoparticles in it (marked with white arrows) (d') Inset displays the magnified open end of the Pt-Fe₂O₃-NS (marked with rectangular box), (e) TEM micrograph of a edge of Pt-Fe₂O₃-NS which shows the graphene sheets rolled (marked with black arrows) with the Pt nanoparticles (marked in white arrows) encapsulated in its core and surface. (f) HRTEM micrographs of Pd-Fe₂O₃-NS illustrating the presence of lattice fringes of graphene. (g) and (g') FESEM-EDX mapping of the selected region (marked in white box) showing the distribution of the Pt element on Pt-Fe₂O₃-NS and (h) XRD diffractograms and (i) Raman spectroscopy of the Pt and Pd-Fe₂O₃-NS fabricated using catalytically active Pt-Fe₂O₃-CNCs and Pd-Fe₂O₃-CNCs as the structural directing templates.
nanoparticles causes reversible faradaic redox reactions on its surface (electrode/electrolyte) introducing pseudo-capacitance behaviour, both of which is expected to act synergistically for enhancement of supercapacitance behaviour. Figure 8(a and b), CV curves of Pt-Fe$_2$O$_3$-NS and Pd-Fe$_2$O$_3$-NS measured at scan rate of 10–100 mV/s, shows asymmetric and quasi-rectangular shape which suggest that the nanochannels present in GNS provides increased charge propagation resulting in improved EDLC properties. With the increased scan rate, absence of any redox peaks or distortions in CV loops suggests its high capacitance retention capacity$^{31}$. The specific
capacitance of GNS is calculated from CV curves using equation, \( C_{sp} = \int \frac{i(t)}{\Delta V} \) \( v \) \( m \), where \( C_{sp} \) is specific capacitance (F/g), \( i \) is average current (A), \( \Delta V \) is potential window, \( v \) is scan rate and \( m \) is mass of electroactive material.\(^{12}\) The specific capacitance of Pt-Fe\(_2\)O\(_3\)-NS, Pt-Fe\(_2\)O\(_3\)-NS and Fe\(_2\)O\(_3\)-NS are calculated as 357, 223 and 152 F/g (at scan rate of 100 mV/s) respectively (Fig. S7(a)), which is significantly higher than the graphene or graphene based scrolls reported in literature.\(^{12,33}\) Figure 8(c), shows the Nyquist plot with vertical slope at lower frequencies and negligible equivalent series resistance at higher frequencies (similar to earlier observations for GNS);\(^{13,31}\) representing ideal capacitive behaviour of the material. The higher \( C_{sp} \) values for Pt-Fe\(_2\)O\(_3\)-NS in comparison to Pt-Fe\(_2\)O\(_3\)-NS is probably due to lowered defects and increased scrolling density which provides efficient pathways for diffusion of ions,\(^{34}\) as evident from the Raman and XRD studies discussed in earlier section. The galvanostatic charge-discharge curves of Pt-Fe\(_2\)O\(_3\)-NS and Pd-Fe\(_2\)O\(_3\)-NS measured at a constant current density of 1 mA/cm\(^2\) are depicted in Fig. S7(b). All the GNS samples exhibited the formation of the triangular shapes with the absence of “IR drop” which suggests their supercapacitive behavior with low internal resistance of electrodes and improved electrode/electrolyte interface, however, shows variation in their charge/discharge time capabilities. The higher charge/discharge time for Pd-Fe\(_2\)O\(_3\)-NS, suggests that due to presence of lower defects, higher surface area and improved scrolling density resulted in the efficient transfer of ions into its nanochannels with the formation of strong EDL layers, which also resulted in significant improvement in performance of supercapacitors.

Further, long term cyclic durability tests retains specific capacitance by ~80.5 and 84.4% after 10000 cycles (charging-discharging between −0.15 to 0.55 V and −0.2 to 0.5 V for Pd-Fe\(_2\)O\(_3\)-NS and Pt-Fe\(_2\)O\(_3\)-NS respectively measured at 1 A/g) (Fig. 8(d)) which shows promising characteristics for practical applications of Pt/Pd-Fe\(_2\)O\(_3\)-NS as electrochemical charge storage devices. The higher retention of specific capacitance (compared to ~76.9% in case of Fe\(_2\)O\(_3\)-NS as shown in Fig. S7(c)) suggests that the nanochannels present in Pt/Pd-Fe\(_2\)O\(_3\)-NS are stable enough providing efficient routes for diffusion of ions alongwith the entrapped catalytically active moieties which are site for multi-electron reversible redox reactions. Therefore, it is envisaged that topological feature of GNS in terms of scrolling density, inter-layer spacings and morphological dimensions can be remotely tuned to enhance EDLC properties followed by encapsulation of variety of catalytical moieties in porous-inter-galleries to induce pseudo-capacitive properties, both of which needs to be optimized such that they could synergistically maximize the supercapacitive behaviour for fabrication of high performance charge storage devices.

**Discussions**

CNCs derived from the renewable resources, acts as a unique template for fabrication of GNS with tunable morphologies ranging from micron to nanoscale dimensions (in length), which are otherwise difficult to control by traditional routes of GNS processing. Through strategic surface modification of CNCs, catalytically active metallic nanoparticles can be incorporated in GNS core (with desired loadings), tunable inter-layer spacings and scrolling density depending upon the targeted applications. From molecular simulation studies, it was observed that formation of GNS using Fe\(_2\)O\(_3\)-CNCs as templates is a thermodynamically favourable process which undergoes self-assembly in the presence of van der Waals forces and \( \pi-\pi \) interactions that are found to depend on several parameters such as density of maghemite nanoparticles, magnetic moment, morphology and dimension of CNCs. The metal nanoparticle encapsulated GNS with unique structural properties and physico-chemical characteristics shows potential applications in fabrication of enhanced hydrogen storage devices and supercapacitors possessing long-term cyclic stability (of ~10000 cycles). The utilization of biobased CNC precursors for fabrication of GNS with tunable morphology, controlled dimensions alongwith the encapsulation of metallic nanoparticles, opens up plethora of multifunctional applications of GNS in diverse platforms with promising commercial opportunities.

**Materials and Methods**

**Materials.** Expandable graphite (EG, 99.9%) purchased from Asbury Carbons (USA) was used for fabrication of graphene. The chemical reagents such as sodium borohydride (NaBH\(_4\)) (>99% purity), hydrogen peroxide (30%), ferric (III) chloride (>96%), 4-nitrophenol (4-NP), sodium hydroxide (NaOH) (>97%), sodium hypochlorite (4%), and sulphuric acid (>99%), (Analytical Grade (AR)) used in the study were obtained from SISCO Research laboratories (SRL Chemicals, India). Bamboo pulp, was selected as the initial cellulosic precursor for the fabrication of CNCs, which was received from Hindustan Paper Corporation Limited (HPCL, Assam, India). The platinum (PtCl\(_2\)) (99.9%) and palladium chloride (PdCl\(_2\)) (99%) salts used in this study were purchased from Sigma Aldrich, India.

**Fabrication of Magnetic cellulose nanocrystals (Fe\(_2\)O\(_3\)-CNCs).** CNCs were fabricated from the bamboo pulp through soda pulping cum bleaching pretreatments (to extract the purified cellulose) followed by stringent sulphuric acid (64 wt%) hydrolysis, as per our earlier reported studies.\(^{15}\) FeCl\(_3\) (2.0 g), was selected as initial iron precursor and dispersed into CNC suspension (1.0 g in 50 ml of ~1 wt% NaOH solution) through sonication at an amplitude of ~30% for 5 min. The dispersed iron salt-CNC suspensions was stirred for ~3 hours at 80 °C purged under inert nitrogen gas flow for ~3 hours to remove the trace amount of oxygen, as per the protocol reported in our earlier studies.\(^{23,36}\) The precipitation of iron nanoparticles was carried out by dropwise addition of the reducing agent, sodium borohydride (~50 mg/ml) under vigorous stirring (~500 rpm) at a temperature of ~90 °C. After ~6 hours, the iron salt-CNC suspension turned black suggesting the completion of reaction and was separated using permanent magnets followed by washing it with ethanol (for three times) and drying (at 50 °C in vacuum oven) to obtain the powdered form of Fe\(_2\)O\(_3\)-CNCs. Fe\(_2\)O\(_3\)-CNCs with higher aspect ratio were fabricated using CNCs derived from filter paper as initial cellulosic precursor following similar protocol for precipitation of iron nanoparticles as mentioned above. The detailed data for its characterization is available in the Supporting Information (Part I).
Fabrication of graphene nanoscrolls (GNS) using Fe₂O₃-CNCs as templates. Graphene was fabricated through thermal exfoliation of expandable graphite with the optimized conditions mentioned in our earlier study. The obtained graphene (~500 mg) was dispersed into methanol followed by its sonication (at amplitude of ~30%) for duration of ~30 mins in presence of the hydrogen peroxide (~2wt.%) as per the literature to introduce epoxy and hydroxyl functionalities.

Epoxidation of Fe₂O₃-CNCs was carried out through reaction of Fe₂O₃-CNCs (~50 mg dispersed in ~20 ml of water through sonication at an amplitude of ~30% for 5 min) with excess epichlorohydrin (~5 ml), at a temperature of ~85 °C for ~4 hours. The epichlorohydrin modified Fe₂O₃-CNCs, was washed with water and ethanol (for ~3 times) to remove the unreacted components, followed by drying (at 50 °C in vacuum oven).

Fabrication of GNS using Fe₂O₃-CNCs as templates was carried out through reaction of epoxidized Fe₂O₃-CNCs with partially oxidized GRO (at a ratio of 1:1 dispersed in 50 ml methanol) at a temperature of 90 °C under reflux conditions which leads to covalent coupling between the two systems. The reaction was continued for ~6 hours followed by washing with ethanol (~3 times) and then subjected to controlled calcination.

The calcination process was carried out in muffle furnace (samples placed in a silica crucible) with controlled temperature program of: 200 °C for 2 hours, 400 °C for 2 hours and 600 °C for 15 mins. Similar protocol was followed for fabrication of Fe₂O₃-NS with higher aspect ratio. The fabricated GNS are designated as Fe₂O₃-NS-HR and Fe₂O₃-NS-LR with high and low aspect ratio respectively, with the encapsulated iron oxide nanoparticles in core of GNS.

Fabrication of platinum and palladium modified magnetic cellulose nanocrystals (Pt-Fe₂O₃-CNCs and Pd-Fe₂O₃-CNCs). Platinum and palladium nanoparticles modified Fe₂O₃-CNCs were fabricated through precipitation of the platinum and palladium chloride salts using sodium borohydride as reducing agent under inert conditions. A homogenous dispersion of Fe₂O₃-CNCs (of low aspect ratio) was formed by dissolving PtCl₃ and PdCl₂ (~50 mg) salts in slightly acidic water, through sonication (~5 min) followed by stirring at ~500 rpm for 3 hours at 80 °C which led to formation of light/grayish/brownish coloration. The impregnated salts on the surface of Fe₂O₃-CNCs were precipitated through dropwise addition of NaBH₄ solution under vigorous stirring (~500 rpm) at a temperature of ~90 °C for 4 hours which subsequently led to formation of grey-black coloration.

Fabrication of graphene nanoscrolls using Pt-Fe₂O₃-CNCs and Pd-Fe₂O₃-CNCs as templates. Pt-Fe₂O₃-CNCs and Pd-Fe₂O₃-CNCs (~20 mg/ml in water) was epoxidized following the similar protocol as mentioned above through reaction with epichlorohydrin for ~6 hours at ~85 °C. The scrolling of graphene sheets was carried out through reaction of epoxidized Pt-Fe₂O₃-CNCs or Pd-Fe₂O₃-CNCs (~50 mg dispersed in methanol) with GRO (~50 mg) at a temperature of 90 °C under reflux conditions for ~6 hours. After the reaction is complete, samples were centrifuged to obtain the precipitate followed by its washing (with ethanol) and drying. The obtained dried samples were placed on a silica crucible and calcined in a muffle furnace to remove the CNCs from its inner core following the similar temperature program as mentioned above. The fabricated samples are designated as Pd-Fe₂O₃-NS and Pt-Fe₂O₃-NS, with the encapsulated Pt and Pd nanoparticles in GNS.

Molecular dynamics simulations of graphene nanoscroll formation. Molecular dynamics (MD) simulation of the scrolling of graphene sheets onto Fe₂O₃-CNC as substrate was carried out using the Discover module of the Materials Studio 7.0 software package. In this work, we have used universal force field (UFF) to describe the interatomic interactions between the graphene sheet and Fe₂O₃-CNCs. The MD simulation was performed in the NVT ensemble at 298 K for a total simulation time of ~500 ps with a time step of 1 fs. The data were recorded every 1 ps to determine the changes in the trajectory of atoms. The Nosé-Hoover thermostat was used to maintain the temperature constant. Further, the van der Waals interactions between the graphene sheets and Fe₂O₃-CNC were calculated with a cut-off distance of 9.5 Å. The electrostatic interactions were calculated using the Ewald summation method with the same cut-off distance of 9.5 Å. It should be noted that geometry optimization was carried out on all the prepared structures namely the graphene sheet, Fe₂O₃-CNC, and Fe₂O₃-CNC/graphene system before starting the MD simulation.

Instrumentation and characterizations. The powder X-ray diffraction (XRD) of fabricated nanoscrolls was recorded with D8 Advance diffractometer (Bruker, Germany) utilizing Cu-Kα radiation (λ = 0.1541 nm) as X-ray source (40kV, 40 mA) measured at scan rate of 0.05° per 0.5 s. To determine the 2θ range ~5–70°. The chemical functionalities in graphene nanoscrolls were analyzed by Raman spectroscopy using Horiba Jobin Yvon (LabRam HR, Japan) equipped with a 1 W, 1064 nm Nd:YAG diode-pumped laser at an excitation wavelength of 514 nm, exposure time of ~5secs and 1024 scans. The surface area was calculated through Brunauer–Emmett–Teller (BET) method based on nitrogen adsorption-desorption at 77 K using a Beckman Coulter surface area analyzer (Coulter SA 3100, USA). Prior to nitrogen physisorption, the nanoscrolls were degassed at 393 K for 2 hours to remove the adsorbed moisture. Morphological dimensions and structure of the fabricated nanoscrolls were characterized using TEM micrographs, high resolution TEM (HRTEM) and selected area electron diffraction (SAED) patterns. The uniformly dispersed graphene nanoscrolls suspensions (in methanol) were drop cast onto carbon-coated grids (Tedpall, USA) and vacuum dried overnight at 60 °C. Images were captured using JEOL JEM 2100 TEM at an accelerating voltage of 200 kV, and the average dimensions were determined (using ImageJ software). The graphene nanoscrolls samples were coated with gold sputtering unit and the morphology was characterized using Field Emission SEM (FESEM) (Zeiss, Germany, Model Sigma) at an accelerating voltage of 2–20 kV. The compositional analysis and mapping of the Pd and Pt nanoparticles in GNS were determined through energy dispersive X-ray analysis (EDX) (Oxford Instruments, UK) at an accelerating voltage of 20 kV using Aztec software.
Hydrogen uptake measurements. Hydrogen uptake by Pd-Fe₂O₃-NS and Pt-Fe₂O₃-NS are measured over a varied pressure range using temperature programmed volumetric sorption apparatus (Model: Isorb-HP, Make: Quantachrome). Prior to analysis the samples were initially outgassed at 150 °C for 30 min in presence of inert gas flow. Subsequently, the hydrogen was allowed to adsorb on the samples at a constant temperature of ~273 K with increasing pressure from 0 to 20 bar. Similarly, desorption of absorbed hydrogen was allowed to occur with the declining pressure maintained at a constant temperature.

Electrochemical performance and measurements. The working electrode was fabricated by dispersing GNS (~6 mg) into iso-propyl alcohol with addition of binder 5% Nafion solution, followed by coating on Toray carbon paper (1 cm²) and drying at 90 °C for overnight. The electrochemical measurements, cyclic voltammetry (CV) (at scan rate: 10–100 mV/s and voltage: 0.2 to 0.6 V), galvanostatic charge-discharge (GCD) and electrical impedance spectroscopy (EIS) (frequency range: 0.01 Hz–10 kHz) were measured using electrochemical workstation Metrohm Autolab PGSTAT 204 operated with a three electrode system, (reference electrode: Ag/AgCl/3 M KCl and counter electrode: platinum) in presence of 0.5 M KOH as electrolyte solution.

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Author Contributions

P.D. performed both the experimental and simulation studies alongwith the electron microscopy imaging, analyzed the data and wrote the manuscript. S.S.G. took part in synthesis and carried out the electrochemical studies. A.K. and V.K. supervised the whole project, guided in theoretical analysis of results and writing of manuscript. All authors took part in discussion of the results and reviewed the finalized form of the manuscript.

Additional Information

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