Graphene Based Coronal Hybrids For Enhanced Energy Storage

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Graphical Abstract
Abstract

Functional materials with designer morphologies are anticipated to be the next generation materials for energy storage applications. In this manuscript, we have developed a holistic approach to enhance the surface area and hence the properties of nanostructures by synthesizing coronal nanohybrids of graphene. These nanohybrids provide distinctive advantages in terms of performance and stability over vertically stacked nanocomposites reported in literature. Various double hydroxide materials self assembled as coronal lamellae on graphene shells have been synthesized and systematically studied. These coronal nanohybrids result in about three-fold increase in energy storage capacity as compared to their traditionally synthesized nanocomposite counterparts. The 3D graphene based nano fibrils in the synthesized coronal nanohybrids provide mechanical support and connect the nodes of the double hydroxide lattices to inhibit restacking. Complex morphologies such as coronal nanostructures increase the interaction surface of the nanostructure significantly. Such an approach is also expected to bring a paradigm shift in development of functional materials for various applications such as sensors, energy storage, catalysis etc.

Keywords - Chemical Nanotechnology, Coronal Nanohybrids, Supercapacitor, Electrochemical Characterization, rGO.
1. Introduction

Engineering morphologies of nanostructures by combining diverse configurations to enhance material properties is an effective approach to synthesize advanced functional materials. The design of novel and sophisticated architectures however requires various innovative approaches. Such designer morphologies provide distinctive advantages in terms of performance and stability over traditionally synthesized nano-composites. Impending innovations in 2D materials are expected to involve expansion of compositional chemistry of interfacial layers [1-3]. Incidentally, incorporation of low-dimensional materials with carbon based nanostructures is an effective approach for synthesizing materials and offers combined advantages of both [4-6]. Amongst various low-dimensional materials, 2D materials such as layered double hydroxides (LDHs) have demonstrated great potential to form nanocomposites with many functional nanomaterials [7-12]. These are inorganic clays of layered materials with positively charged brucite-like layers and posses several interesting features such as tuneability in composition, structure, morphology. However, there are several challenges associated with the stability and energy storage in nanostructures using LDHs. They aggregate easily [13,14] resulting in compromised the energy storage capacity, lack of conductivity and instability [15]. This leads to parasitic reactions resulting in constrained electrochemical performance. Thus, a strategic approach needs to be developed to design and synthesize smart material architectures. Recent progress in the synthesis of graphene [16, 17] based hybrid materials have resulted in a plethora of composites. The major bottleneck is the restacking of the composites with no persistent distinctive nanostructured features [18, 19]. These issues can be mitigated by controlled synthesis of core shell materials to develop distinctive and non-traditional graphene frameworks similar to holey graphene [20] or crumpled graphene nanonetworks [21]. Thus one can exploit these designer nano hybrids to their full potential [22].
In this perspective, we have developed a holistic approach in designing and synthesizing 3D coronal architectures of hybrid materials with porous graphene (PG) based nanowebs. These obliterate the boundaries between inorganic LDH materials that exhibit bulk redox reactions [23-25] and carbon materials that accumulate charge owing to the surface limited processes [26-28]. These architectures are synthesized with controlled geometry by encapsulating coronal hybrids of ultrathin LDH nanosheets of high redox activity, self-assembled radially over functionalized graphene shells, with complementary functionalities. The structural features of coronal hybrids with graphene-based nanostructures introduce reversible wettability and modulation of the chemical potentials with improved rate capability. Additionally, the strain produced in the coronal hybrids due to induced cycling procedures can be relaxed due to the corrugations present on the graphene-based nanonetworks. High resolution STEM and TEM micrographs show evidence of coronal structural features. Comparative electrochemical studies suggests that synthesized coronal hybrids demonstrate good electrochemical stability, rate capability, better electrochemical performance along with enhanced threefold increase in charge storage as compared to their traditionally synthesized counterparts. X-Ray Diffraction (XRD), X-ray photoelectron spectroscopy (XPS) analysis and elementally mapped micrographs suggests fine control over the hierarchical structure of the LDH materials. These structures are highly desirable owing to their ability to control the ionic interactions in an electrode-electrolyte interface. Such interactions have been tailored through porous 3D graphene like nanowebs (3D-PG) which not only prevents restacking but also introduce redox-active organic groups that can electronically communicate with the LDHs. Thus, these nanoarchitectures are expected to create a paradigm shift in development of materials not only for energy storage applications but also others, where surface interactions are extremely crucial, such as catalysis [29, 30], sensors [31, 32], drug delivery [33, 34] and flame retardants [35, 36] etc.
2. Experimental Section

2.1 Synthesis of 3D-coronal hybrids of Co-Mn LDH@PG, Ni-Mn LDH@PG and Ni-Co LDH@PG

Graphene oxide (GO) shells are synthesized using template assisted synthesis route, prior to the self-assembly process of coronal lamellae to for coronal hybrids. GO solution (detailed procedure for GO synthesis is provided in supplementary information as MT-1) is taken and refluxed in a beaker. A mixture of porous silica spheres (0.8 g) (synthesis of porous SiO₂ spheres is detailed in supplementary information as MT-2) and DMF solution (50 mL) is sonicated in a round bottom flask for about 1 hour using an ultra-probe sonicator. Subsequently, (3-Aminopropyl) triethoxysilane is added to this flask. The flask is placed in an oil bath and the temperature of the solution is raised to 110-120 °C. GO solution (1mg mL⁻¹) along with Dicyclohexylcarbodiimide (2.5g) is added to this silica suspension. The reaction mixture then is continuously stirred for 24 hrs to obtain core shells of GO coated over silica nanospheres.

To obtain the coronal nanohybrids of LDHs, the GO coated silica core shell templates were dispersed in 50 mL alcoholic emulsion and sonicated for about 30 minutes. Hexamine (0.56 g) is added to the alcoholic emulsion and sonicated for another 30 minutes. The metallic nitrate precursors (Nickel nitrate hexahydrate, Cobalt nitrate hexahydrate or Manganese nitrate tetrahydrate) are added for synthesis of their respective LDHs. These are taken with a trivalent metal ratio maintained closely around 0.2-0.3. Later, the obtained solution is sealed in an autoclave reactor vessel with reaction temperature maintained at 90°C for 12 hours. The final product is obtained after washing the samples with water and ethanol several times using centrifugation. In order to perform comparative study, the pristine LDH samples were also prepared under same conditions of temperature and concentration.
2.2 Characterizations

The surface morphology of the synthesized nanostructures was imaged using a field-emission scanning electron microscope (FEG-SEM, JEOL JSM-7600F FEG-SEM) and high-resolution transmission electron microscope (HR-TEM) equipped with an energy dispersive X-ray spectroscopy (EDS) (Thermo Scientific, Themis 300 G3) detector. The crystal structure of the samples was investigated using powdered X-ray diffraction (XRD) technique in the 2θ range of 5-80° at a scan speed of 4 min\(^{-1}\) (Panalytical X’Pert Pro with Cu Kα irradiation at a wavelength of 0.1542 nm). The surface chemical composition and valence states were examined using X-ray photoelectron spectroscopy (XPS) (AXIS SUPRA) with an Al Kα radiation. To identify the functional groups, FTIR spectroscopy was performed using 3000 Hyperion Microscope with Vertex 80 FTIR System (Bruker). The vibrational modes of the samples were investigated using Raman spectroscopy (HR-800-UV confocal micro-Raman spectrometer). The N\(_2\) adsorption-desorption isotherms and pore size distribution of the samples were measured using a Brunauer-Emmett-Teller (BET) surface analyser (Quantachrome, Autosorb).

The electrochemical studies were performed using Bio-Logic SP-300 Potentiogalvanostat. The electrochemical evaluations were carried out using cyclic voltammetry, galvanostatic charge-discharge studies and impedance spectroscopy using a three electrode configuration in 3 M aqueous KOH solution as an electrolyte. A platinum mesh with a cross sectional area of 1*1 cm\(^2\) and thickness of 0.1 mm was used as the counter electrode during the measurements. Ag/AgCl was used as reference electrode for the measurements. The working electrodes were fabricated using the active materials, conductive carbon black and polyvinylidene fluoride (binding agent) in a weight percentage of 75:20:5 respectively. The slurry made using these ingredients was pasted on to a Ni substrate and dried overnight in vacuum chamber. The specific capacities were calculated from galvanostatic charge
discharge profiles using the equation, \( C_s = \frac{Q}{m} \). Here \( C_s \) is specific capacity (C\( g^{-1} \)), \( Q = I_d t_d \), \( t_d \) is the discharge period (s), \( I_d \) is the constant discharge current (A) and \( m \) is the active mass loading of each electrode.

3. Results and discussion

3.1 Bio-mimetic 3D-spherical coronal hybrids and characterizations

**Figure 1.** Schematic showing synthesis of 3D-networked coronal hybrid nanostructures of LDH on PG shells using hydrothermal reaction. Synthesis involves growth of LDH lamellae in form of corona over the PG shell using surface functionalization forming reduced graphene oxide. Synthesis involves acylation and encapsulation mechanism via the electrostatic assembly over the fibrous silica particles in the initial stage of the assembly. Final growth stage involves ultrathin LDH nanosheets radially grafted over the PG skeletal structures. High resolution TEM images are used to understand the synthesis process. The LDH formation mechanism from bivalent and trivalent metallic cations and the XRD patterns of pristine and coronal hybrids of LDHs is presented.
The synthesis of coronal nanohybrids wrapped in intricate nanowebs requires a soft template-based approach. A schematic showing detailed synthesis protocol of these nanostructures is shown in Figure 1. In order to achieve this, silica nanoparticles were injected into a solvent medium under agitation with oxidized graphene. This resulted in interfacial growth of GO shells on the silica spheres due to acylation mechanism and formed uniform dispersion. These were then separated by centrifugation. Subsequently LDH nanosheets self-assemble during hydrothermal reaction over the SiO$_2$/GO core shell structures and overtime coronal hybrid assemblies along with 3D fibrillar graphene like nanowebs were produced. The SiO$_2$ etches out self sacrificially resulting in formation of reduced graphene oxide (rGO) shells. This method has been used to demonstrate synthesis of three representative configurations of transition metal coronal hybrid structures i.e. Co-Mn LDH, Ni-Mn LDH and Ni-Co LDH self-assembled over GO shells embedded in a PG network. Carefully designed porous silica core assists in the structure-building and are eventually etched off.

The crystallographic structure of the synthesized hybrid coronal nanostructures was obtained by analysing the XRD pattern. The crystallographic signatures of coronal hybrids are compared with corresponding pristine LDH nanosheets. The diffraction patterns obtained for the coronal hybrid samples (represented as Co-Mn LDH@3D-PG, Ni-Mn LDH@3D-PG, and Ni-Co LDH@3D-PG) showed features similar to that of typical hydrotalcite-like structure with the Braggs reflections assigned to (003), (006) and (009)/(012) planes. These showed good agreement with diffraction patterns of the pristine LDHs (represented as Co-Mn LDH, Ni-Mn LDH and Ni-Co LDH) as well. The diffraction patterns for the LDHs exhibited a rhombohedral (3R-type polytype) stacking sequence with $R3m$ symmetry. However, the diffraction peaks of graphene like nanostructures are not apparent in the XRD patterns of hybrid material because of highly dense coronal LDH lamellae on the surface of ultra-thin
rGO shells. The lattice parameters along with the tuned basal spacing for various hybrid and pristine LDH samples obtained from XRD measurements have been tabulated in table 1 below.

Table 1. Calculated lattice parameters and crystallite sizes for the pristine LDH and hybrid samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Lattice parameters (Å)</th>
<th></th>
<th>Crystallite Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>d(003)</td>
<td>d(006)</td>
<td>d(009)/(012)</td>
</tr>
<tr>
<td>Co-Mn LDH</td>
<td>9.17</td>
<td>4.67</td>
<td>2.73</td>
</tr>
<tr>
<td>Co-Mn LDH @3D-PG</td>
<td>9.12</td>
<td>4.58</td>
<td>2.69</td>
</tr>
<tr>
<td>Ni-Mn LDH</td>
<td>7.42</td>
<td>3.71</td>
<td>2.60</td>
</tr>
<tr>
<td>Ni-Mn LDH @3D-PG</td>
<td>7.16</td>
<td>3.57</td>
<td>2.53</td>
</tr>
<tr>
<td>Ni-Co LDH</td>
<td>9.37</td>
<td>4.69</td>
<td>3.14</td>
</tr>
<tr>
<td>Ni-Co LDH @3D-PG</td>
<td>9.20</td>
<td>4.65</td>
<td>3.10</td>
</tr>
</tbody>
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The homogenously layered cationic distribution in the synthesized nanostructures is assisted by electrostatic interaction of the cationic layers [3,38]. It is understood to be a major factor that favours the crystallization of LDHs. The lattice parameters depend on various factors such as size and amount of interlayer anions, hydration, cation–cation separation [39,40]. Further, the presence of possible heterogeneity in finely dispersed crystalline LDHs with some order-disorder in cationic distributions cannot be ignored [41,42]. The inter-planar spacing is finely tuned with the different compositions. The type of anions intercalated between the interlayers can be controlled by restricting the type and quantity of reagents. The
crystallite size obtained from XRD measurements show that the hybrids have a smaller crystallite size as compared to that of pristine LDHs.

Figure 2. (a) High resolution STEM image showing assembled spherical coronal LDH nano lamellae over the porous rGO shell. (b) FEG-SEM image shows the morphologically stable structure of final spherical coronal nanohybrids. (c) Magnified SEM micrograph showing open porous channels on the surface of the coronal hybrid. (d) High resolution STEM image shows 3D-PG shells. (e) Shows the Raman spectra for Co-Mn LDH@3D-PG, Ni-Mn LDH@3D-PG and Ni-Co LDH@3D-PG respectively and (f)-(h) shows high resolution image showing diffraction fringes matched with their
The small LDH crystallites assemble uniformly over the 3D-PG skeletal structure that enables access to all active intercalation sites, leading to high specific capacities and fast ion diffusion [43]. However, due to extreme proximity of the LDH nanosheets, the 3D-PG signal was too weak to be observed in XRD.

The surface morphology of representative spherical coronal nanohybrid assemblies of Ni-Mn, Co-Mn and Ni-Co LDH shown in Figure 2(a) is imaged in STEM mode using high resolution TEM. The high-resolution STEM micrographs show 3D radial arrangement of nanostructured LDH lamellae radially assembled over the surface of PG core. After the self-assembly of LDH lamellae on the surface functionalized graphene, the core shell architecture exhibits the morphology of a spherical coronal structure with a large number of open porous channels which is evident from the FEG-SEM images shown in Figure 2(b) and 2(c) respectively. The inner layers through chemical moieties present on the backbone of graphene like nano-webs with a robust 3D architecture has micro and meso-porous features that are capable of guiding the electrons along desired and predetermined paths as understood from Figure 2(d). The micrographs also suggest that the LDHs are radially self-assembled on rGO shell. During the process of formation of 3D-PG nanowebs, the remnant oxygen functionalities on graphene sheets act as pillars to provide a relatively large interlayer spacing while the sp² clusters that are connected across the interfacial layers form a porous network. Eventually, these nanowebs enhance the ionic current and electronic current conduction rate. In addition to these images, respective FEG-SEM and HR-STEM micrographs for pristine Co-Mn LDH, Ni-Mn LDH and Ni-Co LDH and hybrid nanostructures of Co-Mn LDH@3D-PG, Ni-Mn LDH@3D-PG and Ni-Co LDH@3D-PG are shown as Supplementary Figure S1 and S2. Raman spectroscopy is performed to confirm the minor modifications in the
properties of the synthesized nanohybrids. Figure 2(e) shows the representative Raman spectra of Co-Mn LDH@3D-PG, Ni-Mn LDH@3D-PG, and Ni-Co LDH@3D-PG samples. Graphene has two distinctive vibrational modes corresponding to the 'D' band (1350 cm\(^{-1}\)) which is related to phonons at 'K' point with \(A_{1g}\) symmetry and are linked with structural defects. The 'G' band (1580 cm\(^{-1}\)) can be identified with phonons near the zone centre with \(E_{2g}\) symmetry, this suggests the presence of \(sp^2\) hybridized carbons [44]. Raman spectrum for hybrid samples shows the presence of Raman signature corresponding to graphene like core structures with a ‘G’ and ‘D’ bands. The ratio of intensity of ‘D’ to ‘G’ bands (\(I_D/I_G\)) in all hybrids of LDH@3D-PGs is observed to increase from 0.9 (for the prepared GO) to 1.24 for Co-Mn LDH@3D-PG, 1.38 for Ni-Mn LDH@3D-PG and 1.31 for Ni-Co LDH@3D-PG, showing the prominence of the architectural composition in size reduction of \(sp^2\) in-plane domains. As a consequence, there is also a disorientation in the crystal structure of 3D-PG through cross-linking of LDH lamellae [45]. The shifts observed in the Raman spectra suggests that more localized \(sp^3\) defects are introduced into the \(sp^2\) carbon structure [46]. Briefly, there is an additional disturbance in the \(sp^2\) carbon network with the introduction of LDH lamellae. This is expected to exceptionally improve the electrochemical performance through interactive charge transfer between the LDHs and 3D-PGs. These conclusions are also in good agreement with diffraction fringes for the nano-hybrids taken at radially aligned locations as shown in Figures 2(f) - 2(h) for the three LDH variants. The inter-planar spacing calculated from selected area electron diffraction (SAED) patterns obtained using HR-TEM are also indexed to the lattice planes of respective LDH hybrids (Supplementary Figure S3). Additionally, the findings from Fourier transform infrared spectroscopy (Supplementary Figure S4) concur with the conclusions drawn from Raman analysis, suggesting the presence of un-oxidized graphitic skeletal vibrations and bending mode of carbonyl stretching vibrations of carbon in the hybrid samples.
The homogeneity of elemental distribution in the synthesized samples is investigated using EDS. The elemental composition for the pristine LDH materials (Co-Mn LDH, Ni-Mn LDH and Ni-Co LDH) and the hybrid LDH materials (Co-Mn LDH@3D-PG, Ni-Mn LDH@3D-PG and Ni-Co LDH@3D-PG) is mapped in Figure 3. The high-resolution STEM mapped regions, suggests uniform distribution of the transition elements (Ni, Co and Mn) in the LDH lamellae over the 3D-PG skeletal structures. The pristine LDHs shows only the metallic components. The synthesized coronal nanohybrids exhibit strong signature of the C and O elements in the interior portion with branched network like features which reveals that the core position has no conglomerations as also concluded from the elemental maps. The pristine LDH nanosheets on the other hand aggregates to form large size clusters of nanosheets which are cross-linked in a disordered fashion as shown in Supplementary Figure S5. Moreover, the pristine LDH nanosheets looks rickety with no open porous structures, which results in poor ionic transfer. These findings are in good agreement with our discussions and our results provides significant improvement over those reported in literature, where the LDHs eventually agglomerate and deposit on the carbon surface (GO or rGO).
Figure 3. EDS maps for various elements obtained on high resolution STEM images horizontally aligned from left to right (a) Maps of Co-Mn LDH@3D-PG; (b) Maps of Ni-Mn LDH@3D-PG; (c) Maps of Ni-Co LDH@3D-PG. XPS spectra obtained for coronal nanohybrid architectures (left to right); (d), (e) & (f) - XPS spectra for Co-Mn LDH@3D-PG; (g), (h) & (i) - XPS spectra for Ni-Mn LDH@3D-PG; and (j), (k) & (l) - XPS spectra for Ni-Co LDH@3D-PG samples.

High resolution XPS spectra of all the three coronal hybrids variants were evaluated to investigate the chemical composition as well as the valence states of individual elements. The C1s spectra was de-convoluted to reveal the organic compositional state of graphene oxide core shells. The high-resolution spectra of Ni 2p showed two major peaks besides satellite peaks originating from Ni$^{2+}$ ion signals at 861.2 eV and 879.1 eV. The major peaks associated with both the Ni based LDH hybrid variants showed peaks at ~855.6 eV and 873.3 eV corresponding to Ni 2p$_{3/2}$ and Ni 2p$_{1/2}$ respectively. The high-resolution Mn XPS spectra in Ni-Mn LDH and Co-Mn LDH hybrids showed two major peaks at ~641.7 eV and ~653.3 eV corresponding to Mn 2p$_{3/2}$ and Mn 2p$_{1/2}$. The valance peaks of Mn are further de-convoluted and major contribution from Mn$^{3+}$ oxidation state in the samples dominate. It was revealed that additional valance states of Mn$^{4+}$ and Mn$^{2+}$ were also included in the spectrum. Moreover, for the Co based hybrid LDH variants, two pairs of binding energy peaks were observed corresponding to two spin orbit doublets and two satellite shake ups (~785.9 eV and ~802.9 eV). After de-convolution, one pair of binding energies is assigned to Co$^{3+}$ that are centred at ~780.2 eV and ~795.4 eV and other pair centred at ~782.5 eV and ~797.4 eV corresponds to Co$^{2+}$. This confirms multiple oxidation states of Co species in the hybrid sample. In all the three hybrid samples C1s originating from graphene oxide core shells, which eventually converts to rGO nanostructures, was clearly validated using XPS spectra. It is noticed that graphene oxide is converted to reduced graphene-based nanostructures with a strong C-C peaks at ~284.6 eV. The deconvoluted spectrum showed peaks with considerably low intensity at ~286.2 eV (C-O) and ~288.5 eV (O-C=O) with smaller proportion
confirming effective removal of oxygen functionalities. The reduction rate was understood to be more efficient in Ni-Co LDH@3D-PG compared to other two hybrid systems. On the other hand, the interaction between morphology, conductivity and porosity critically defines the physical and electrochemical properties of the resultant controlled nanostructured materials [47]. The isomorphous substitution of bivalent metallic cations by trivalent ions results in a positively charged framework (otherwise called cationic charged framework) [48]. Ionization of oxygenated functional groups (-OH and -COOH) in GO shells resulted in electrostatic interaction due to difference in electronegativity. Thus, the carbon skeleton strongly binds with LDH lamellae through strong interactions of cationic metallic framework with oxygen-containing functional groups and the cation-π interactions of the same with sp² aromatic cluster. Further, the presence of lone pairs of electrons on oxygen atoms in rGO shells allow the rGO shells to accept more protons. Subsequently, LDHs share a proton (H) with the oxygen sites or π bands of the rGO core shells, establishing a strong resilience with hydrogen bond [49]. Evidently, there are also weak van der Waals interactions between the LDHs and rGO sheets. Thus, the strong interactions between the LDHs and 3D-PG protect the 3D architecture. Therefore, even high values of current densities and repeated cycling was unable to break the interactions between the LDHs and 3D-PG structure with charge storage processes happening due to redox mechanisms in LDHs and charge-adsorption/desorption in 3D-PG.

To have a better understanding of the synthesis process of 3D-PG, HR-TEM micrographs were recorded at various stages of synthesis and are shown in Figure 4. Figure 4(a) shows GO encapsulation over SiO₂ templates, while Figure 4(b) shows 3D-PG frameworks obtained from hydrogel like graphene formed during self-sacrificial removal of silica core. Further, the electron diffraction patterns provided as insets confirmed the transformation of GO nanosheets to rGO based porous nanostructures. Representative
Raman spectrum shown in Figure 4(c) was recorded to support the findings from electron diffraction experiments. Raman data suggests stacking ratio ($I_D/I_G$) of 1.2. FE-SEM micrographs in Figure 4(d) shows 3D open porous structures of graphene based nanonetworks which show porous channels, that helps in improving the accessible surface area. In conventional graphene based nanohybrids, the inter layers irreversibly agglomerate due to strong π-π stacking and van der Waals interactions. This resulted in reduced surface area. This phenomenon is understood to hinder the ion diffusion properties. Thus, in graphene based open porous structures, the accessible surface area and the specific capacitance is enhanced. The open channel structures promote the penetration of electrolytes as well as enable in enhanced adsorption of ions. They also help in reducing mechanical stress/strain caused by the electrochemical reactions. Hence, enhancement in electrochemical activity and kinetics is anticipated. The high surface area of graphene along with presence of substantially large active interfaces are also understood to contribute towards improved performance. Figure 4(e) shows the adsorption-desorption isotherms derived for both pristine as well as coronal nanohybrid samples for representative Ni-Co system. The isotherms exhibit type IV characteristics with a hysteresis loop in the N$_2$ desorption branch and appear at relative pressure of $P/P_0 > 0.4$. This supports the presence of the porous features as concluded from microscopic analysis of our samples.
Figure 4. (a) HR-TEM micrograph showing GO encapsulated SiO$_2$. Bottom right inset shows the SAED pattern obtained from the surface indicated with red arrow pointing towards the left. (b) HR-TEM image of 3D porous graphene obtained via hydrogel formation during self-sacrificial process. Top right inset shows the SAED pattern obtained from the thin surface indicated with red arrow pointing towards right. (c) Raman spectrum of 3D porous graphene structure. (d) FE-SEM image of 3D porous structure of graphene extracted from GO/SiO$_2$ core. (e) Comparison of N$_2$ adsorption/desorption isotherms of pristine Ni-Co LDH and coronal nanohybrid of Ni-Co LDH @3D-PG. (f) Comparison of pore size distribution of pristine Ni-Co LDH and coronal nano hybrid of Ni-Co LDH @3D-PG.
The surface areas of pristine Ni-Co LDH and Ni-Co LDH@3D-PG was calculated to be 20.6 m² g⁻¹ and 195.4 m² g⁻¹ respectively. Further the hysteresis loop for Ni-Co LDH@3D-PG coronal hybrid is of type H3 which is a characteristics of a mesoporous structure. In addition, the pore size distribution is provided in Figure 4(f), which shows large volume of pores in case of the coronal hybrids. The BET measurements suggests that interfacial contact is established between the LDH lamellae and the 3D graphene structures enabling efficient charge transfer mechanism by reducing the ion diffusion length.

3.2 Charge storage mechanism in the coronal hybrid architecture

The 3D-PG nano-networks eases the electrolytic access and enhances the overall specific charge storage capacity compared to the solid matrix or aggregated sheets of the active material as shown in Figure 5(a). The biomimetic 3D graphene backbone provides a good surface area with open porous channels. These enhance the redox active sites and fast transport of ions. This makes the GO coated silica core shells an ideal template for making hybrid nanostructures. The LDH compositions used in synthesis are typically hybrid battery type that exhibit pseudo-capacitive behaviour. The self-assembly of LDH nanosheets on 3D-PG skeletal structure enables in the formation of ordered nanostructures. Transition-metal LDHs not only offer much larger charge storage, but most of them also have low electrical conductivity. The interconnected graphene nano-webs provide high electrical conductivity and chemical stability by synergising the virtues of active materials into a hybrid structure as suggested in Figure 5(b). Moreover, compared to traditional solid and aggregated morphologies, the synthesized coronal nanohybrids aid in shortening the diffusion path of the ions because of their large aspect ratio. They also help ineffective utilization of the active materials. Thus, the coronal nanohybrids with carbon skeletal frameworks acts as mechanical support.
**Figure 5.** (a) Schematic showing ionic and electron charge transfer in solid active material, aggregated LDH nanosheets and hybrid LDHs over 3D-PG nano-webs. (b) Graphics showing distribution of nano webs inside the coronal hybrid and illustrative charge transfer pathways. (c) Comparison of specific capacities of pristine LDHs with their respective coronal nanohybrids, and (d) Schematic illustrating various components inside graphene based coronal hybrid.

It assists in dispersion of the LDH nano sheets to avoid self-aggregation. This helps in creating extra active sites which help in improving the electrochemical performance. Hence, the specific capacity of the hybrid materials is observed approximately three times higher.
than the pristine LDH materials as seen in Figure 5(c). In addition to offering high specific capacity, the perforations in the coronal structures as shown in Figure 4(d) and the nanoweb shaped supports significantly improves the mechanical strength as compared to solid films of the pristine material. Charges are stored from within the electrode bulk to surface involving redox processes that occur orders of magnitude faster and allow greatly improved power densities and enhanced cycle life [50]. The redox reactions involving LDHs with represented bivalent metal ion (M$^{\text{II}}$) and trivalent metallic ion (M$^{\text{III}}$) configuration transform into oxy-hydroxides or/and to oxide under a reversible redox mechanism with Ni, Mn or Co. Additionally, there is an adsorption and desorption phenomenon taking place in the 3D-PG framework shown in the Figure 5(d). The high electronic and ionic conductivities combined with intrinsic strength and flexibility of graphene nanowebs allow structural stability for enhanced energy storage.

### 3.3 Electrochemical evaluation of the hybrid materials

Multi-layered architecture of coronal hybrids significantly enhances the specific surface area along with the porosity. These provide abundant active sites for the migration of ionic species and stimulates the interaction between the electrolyte and active material [51]. Consequently, the coronal hybrids demonstrate higher specific capacity and rate performance compared to the pristine materials. Electrochemical evaluation of pristine Co-Mn LDH, Ni-Mn LDH, Ni-Co LDH and their respective coronal nanohybrids have been investigated in a three-electrode configuration using cyclic voltammetry (CV), galvanostatic charge discharge (GCD) and electrochemical impedance spectroscopy (EIS) measurements. 3M KOH solution is used as electrolyte. A comparison of representative cyclic voltammograms of synthesized pristine LDHs and their coronal nanohybrids are shown in Figures 6(a)-6(c). The CV curves of pristine Co-Mn LDH, Ni-Mn LDH, Ni-Co LDH and their coronal nanohybrids were obtained at a scan rate of 5 mVs$^{-1}$. These show redox peaks during the anodic and cathodic sweeps.
suggesting typical pseudocapacitive behaviour. The CV curves of pristine LDHs and their hybrids show similar profiles, suggesting the occurrence of identical electrochemical processes. The CV curves for the coronal nanohybrid exhibits a large area under the curve suggesting enhanced energy storage. The general equations for the redox processes in the LDH hybrids are shown in Figure 5(d). The Co-Mn LDH and Co-Mn LDH@3D-PG has two redox couples within the potential window of -0.2 V to 0.6 V. Two anodic peaks are observed at ~ 0.1 V and ~0.46 along with two cathodic peaks at ~0.02 and 0.36. The first redox couple is due to reversible Faradaic transition from Mn^{2+}/Mn^{3+} couple and the asymmetric peaks can be associated with a reversible transition from Mn^{3+} to Mn^{4+}. The second redox couple is associated with quasi-reversible conversion of (Co^{2+}/Co^{3+}) and (Co^{3+}/Co^{4+}). A pair of redox peaks are also obvious for Ni-Mn LDH and Ni-Mn LDH@3D-PG signifying active redox environment in these battery-type hybrid materials. Similarly, the area enclosed under CV curve and peak current for the Ni-Mn LDH coronal nanohybrid is much larger as compared to that of pristine Ni-Mn LDH. It is evident that in Ni-Mn LDH@3D-G most of the energy storage and current is achieved in the potential range of 0.2-0.55 V. The net charge stored in the synthesized coronal hybrids also depend on the charge stored not only on the outer surface (i.e. due to LDH lamellae) but also in the inner surface region accessed between the electrolyte and active electrode. The high redox currents with a large enclosed area under the CV curve are realized from reasonable compositional tuning of the coronal hybrids. For instance, coronal hybrid of Co-Mn LDH and Ni-Mn LDH delivered a high specific capacity due to an optimum replacement of Co or Ni by Mn. It is also understood that the structural mitigation by tailoring coronal hybrids using 3D graphene based nanowebs can help in generating a good concentration gradient. However, the Co-Mn LDH@3D-PG delivers a low specific capacity value than Ni-Mn LDH@3D-PG which may be due to highly active Ni^{2+}. During the in-situ growth process, GO shells oxidizes Co^{2+} and Mn^{2+} to trivalent metallic
ions, but Ni$^{2+}$ still remain more stable and assists in enhancement of specific capacity and rate capability. In case of Ni-Co LDH and Ni-Co LDH@3D-PG, both cyclic voltammograms show a pair of redox peaks. Due to the Faradaic reactions, Ni(OH)$_2$ undergoes transition from Ni$^{2+}$ to Ni$^{3+}$. Additionally, two pairs of peaks arise from Co(OH)$_2$ due to redox transition from Co$^{2+}$ to Co$^{3+}$ and Co$^{3+}$ to Co$^{4+}$. The redox peaks are quasi-reversible with a good capacitive behaviour. Most of the charge storage is predominant in the potential range of 0.1-0.4V. In general, the total charge storage enclosed under the CV curves for the hybrids can be governed by three mechanisms: (a) The pseudocapacitive charge storage mechanism due to intercalation/de-intercalation of electrolytic ions, both OH$^-$ ions and K$^+$ ions intercalate/de-intercalate into the interlayer domains of the LDHs which is controlled by the diffusion-limited process [52], (b) The redox reactions over the cationic surfaces of LDHs by electroactive species and (c) The double layer charge storage component, due to charge adsorption/desorption of ions over the 3D-PG frameworks, which could be assigned as a surface-limited process [53]. The redox peak shifts (anodic peak to a higher potential and cathodic peak shift to a lower potential) of LDH@3D-PGs indicates the effect of polarization, which can be attributed due to the phase separation between pristine LDHs and the presence of 3D graphene framework in LDH@3D-PGs. However, it is anticipated that the presence of carbon framework decreases the polarization by improving the electronic conductivity. The other reason behind the peak separation is due to the overall concentration gradient of Ni or Co affected by the presence of GO during the 3D-PG formation[54]. Further, to realize the effect of 3D-PGs and to measure the specific capacities of the pristine LDHs and their hybrids, the samples were characterized using GCD measurements. The specific capacities of all the electrodes were calculated from the charge-discharge curves. A comparative study of the GCD profiles for pristine and coronal hybrids are shown in Figures 6(d) - 6(f). The study was performed in 3M KOH solution at a current density of 1Ag$^{-1}$. The observed potential vs
time response for the synthesized LDH configurations suggest that the Faradaic reactions are highly reversible with charge–discharge coulombic efficiency to be more than ~99 %.

Symmetric triangular profile with well-defined plateaus suggests good capacitive behaviour. One portion of the profile shows a linear discharge profile, indicating a surface-limited charge storage process. The broad extended plateau region represents a major portion of charge storage during discharge due to the redox active species with a low polarization.

**Figure 6.** Comparative cyclic voltammograms of pristine LDH and their coronal hybrids in 3 M KOH solution using three-electrode configuration at a scan rate of 5mV s⁻¹ for (a) Co-Mn LDH and Co-Mn LDH@3D-PG hybrids, (b) Ni-Mn LDH and Ni-Mn LDH@3D-PG and (c) Ni-Co LDH and Ni-Co LDH@3D-PG. Comparative GCD profiles for (d) Co-Mn LDH and Co-Mn LDH@3D-PG hybrids, (e) Ni-Mn LDH and Ni-Mn LDH@3D-PG and (f) Ni-Co LDH and Ni-Co LDH@3D-PG. A comparative of EIS profiles obtained for (g) Co-Mn LDH and Co-Mn LDH@3D-PG hybrids, (h) Ni-Mn LDH and Ni-Mn LDH@3D-PG and (i) Ni-Co LDH and Ni-Co LDH@3D-PG.
The notable deviation in the GCD profiles from a straight line is understood to occur primarily due to the redox reaction mechanisms of nickel or cobalt species. The specific capacities of Co-Mn LDH, Ni-Mn LDH and Ni-Co LDH, calculated from GCD are found to be 250\text{C}\text{g}^{-1}, 314\text{C}\text{g}^{-1} and 361\text{Fg}^{-1} in potentials ranging from -0.2 to 0.6 V, 0 to 0.5 V and 0 to 0.4 V respectively, at a current density of 1 \text{Ag}^{-1} for all the samples. The graphene based coronal hybrids of these pristine LDH materials exhibited an ultra- high specific capacity of 776\text{Cg}^{-1}, 984 \text{Cg}^{-1} and 1056 \text{Cg}^{-1} respectively in the same potential window and at same current density. Approximately, three-fold increase in specific capacity values suggest the vital role played by the morphology of nanostructures in enhancing the charge storage capacity, thereby improving the electrochemical activity of the LDHs.

To further evaluate the electrochemical performance, EIS studies were performed in an open circuit configuration with potential of 10 mV and in a frequency range from 10 mHz to 100 kHz frequency range as shown in Figures 6(g) - 6(i). The EIS spectra of the pristine LDHs were compared with that of the coronal hybrids to understand the impact of morphology on the electronic and ionic transport. The Nyquist plots obtained for all the samples resembled a semicircle in the high frequency domain specifying the charge transfer resistance (\(R_{ct}\)) that makes a horizontal intercept. The \(R_{ct}\) values for the pristine LDH systems are found to be approximately 6.25\,\Omega, 5.05\,\Omega and 1.45\,\Omega for Co-Mn, Ni-Mn and Ni-Co LDH. It is observed that the respective coronal hybrids have \(R_{ct}\) values of approximately 2.70 \,\Omega, 2.25\,\Omega and 0.25\,\Omega. These values show that the coronal hybrids have a relatively smaller diameter of the semicircles (smaller value of \(R_{ct}\)) which signifies the vital role of 3D-PG networks at the electrode-electrolytic interface, with a low ionic resistance of electrolytic species accompanied with good electrical conductivity. Further, the EIS spectra has vertical lines with a phase inclination of above 45° for both the electrode systems in the low frequency range which demonstrates a diffusion-controlled process, otherwise called a
Warburg component. This indicates the Faradaic nature of the charge transfer process. Better ionic diffusion with shorter ionic intercalation pathways for ionic species in the alkaline electrolyte in coronal hybrids is inferred from the relatively higher inclination of the Warburg component. The overall resistance associated with active material/current collector interface and the intrinsic resistance from the electrode material in the electrolyte known from the solution resistance ($R_s$) is represented as a horizontal intersection of each semicircle with the $x$-axis. The $R_s$ values obtained from the EIS measurements are $\sim 0.45\Omega$, $\sim 0.55\Omega$ and $\sim 0.59\Omega$ for the pristine Co-Mn, Ni-Mn and Ni-Co LDH respectively. The values of $R_s$ were found to be similar for the coronal hybrids as well.

Further to give a detailed picture about the electrochemical activity of the coronal hybrids, cyclic voltammograms were recorded at various scan rates. Figure 7(a) - 7(c) shows the CV profiles of the three coronal hybrids obtained at scan rates of 5 mVs$^{-1}$, 10 mVs$^{-1}$, 20 mVs$^{-1}$, 30 mVs$^{-1}$, 40 mVs$^{-1}$ and 50 mVs$^{-1}$. The occurrence of redox peaks in the CV profiles describes the Faradaic nature of the electrodes. The CV profiles for the pristine materials are shown as Supplementary Figure S6. Figure 7 (d) - 7(f) shows the GCD profiles of the coronal hybrid electrodes, obtained at various current densities. The highly reversible Faradaic charge-discharge profiles appear to be mirror images to each other at various current densities suggesting a typical battery-type performance. The coronal hybrid materials have large discharge rates compared to their pristine counterparts.
Figure 7. Cyclic voltammograms of coronal hybrids in 3 M KOH solution using three-electrode configuration at various scan rates (a) for Co-Mn LDH@3D-PG hybrids, (b) for Ni-Mn LDH@3D-PG and (c) for Ni-Co LDH@3D-PG. GCD profiles obtained at various current densities (d) for Co-Mn LDH@3D-PG, (e) for Ni-Mn LDH@3D-PG and (f) for Ni-Co LDH@3D-PG. Specific capacity vs current density profiles obtained at various current densities (g) for Co-Mn LDH@3D-PG (h), for Ni-Mn LDH@3D-PG and (i) for Ni-Co LDH@3D-PG.

The CV and GCD profiles of coronal hybrids represents typical characteristics of a redox material with battery-type behaviour. Hence the higher scan rates result in steeper concentration gradients in turn result in higher diffusive transport of the electrolytic species. The GCD profiles of pristine LDHs are shown in Supplementary Figure S6(d) - S6(f) at various high current densities. An increase in the discharge current densities accompanied
with a gradual decrease in the specific capacities is due to fast acting Faradaic reactions that drive incomplete utilization of electrode material. Hence, during the fast intercalation/de-intercalation process in LDHs, at higher charge-discharge rates the H$^+$ ionic transport is limited to the solid interface and the interaction or the reactivity of H$^+$ with the hydroxyl ions is also limited. The coronal hybrid electrodes exhibit a maximum specific capacity at 1 Ag$^{-1}$ and still retains high specific capacity of 300 Cg$^{-1}$, 505 Cg$^{-1}$ and 755 Cg$^{-1}$ at 5 Ag$^{-1}$ for Co-Mn LDH@3D-PG, Ni-Mn LDH@3D-PG and Ni-Co LDH@3D-PG respectively as illustrated in Figures 7 (g) - 7(i). The cyclic stability profiles of coronal hybrids for about 4000 cycles are presented in Supplementary Figure S7. The battery-type characteristics of the graphene coronal hybrids are finely regulated with tuneable inter-layer spacing, composition and interfacial chemistry of LDHs with graphene based nanowebs. As a consequence, the enhanced battery-type property with a notable specific capacity is still persistent even at high current densities.

4. Conclusion

To sum up, graphene based designer nanohybrids in form of coronal morphologies have been synthesised with Co-Mn, Ni-Mn and Ni-Co LDH lamellae self-assembled radially outwards as corona on the surface of rGO shells connected by porous graphene networks. The well-tailored nano-design, with tuneable interlayer spacing along with modification of the interfacial chemistry with interconnected 3D-graphene like nano-web structures supplement better electronic and ionic conductivities. This in turn leads to low internal resistance that enables in fast charge transfer process with enhanced electrochemical stability. The 3D-PGs are mechanically robust structures and enable the electrodes in tolerating high charging currents. This results in higher energy and power densities in coronal hybrids as compared to pristine and stacked composites reported in literature. The efficient and strategic approach to develop coronal hybrids takes into account the tuneable compositional and structural features.
of the transition metal layered double hydroxide materials (Ni, Co or Mn) with well-connected 3D-PG nanoweb architectures that have yielded a high specific capacity. The high rate capability is understood to be due to highly percolated 3D-PGs inside the coronal sphere with radially aligned ultrathin LDH nanostructures. This newly developed nanohybrids can deliver high specific capacities of 776Cg⁻¹, 984Cg⁻¹ and 1056Cg⁻¹ for Co-Mn LDH@3DPG, Ni-Mn LDH@3DPG and Ni-Co LDH@3DPG respectively with outstanding rate capability. The holistic design approach in tailoring the morphologies of energy storage materials can lead to the rational design and development of a wide range of functional materials for higher energy and power densities for energy storage applications.

Conflicts of interest
The authors declare no conflict of financial interests or personal relationships that could give the impression to influence this work.

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