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Development of a Coaxial 3D Printing Platform for Biofabrication of Implantable Islet-Containing Constructs

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Abstract
Over the last two decades, pancreatic islet transplantations have become a promising treatment for Type I diabetes. However, although providing a consistent and sustained exogenous insulin supply, there are a number of limitations hindering the widespread application of this approach. These include the lack of sufficient vasculature and allogeneic immune attacks after transplantation, which both contribute to poor cell survival rates. Here, these issues are addressed using a biofabrication approach. An alginate/gelatin-based bioink formulation is optimized for islet and islet-related cell encapsulation and 3D printing. In addition, a custom-designed coaxial printer is developed for 3D printing of multicellular islet-containing constructs. In this work, the ability to fabricate 3D constructs with precise control over the distribution of multiple cell types is demonstrated. In addition, it is shown that the viability of pancreatic islets is well maintained after the 3D printing process. Taken together, these results represent the first step toward an improved vehicle for islet transplantation and a potential novel strategy to treat Type I diabetes.

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Nanoarchitectured Nitrogen-Doped Graphene/Carbon Nanotube as High Performance Electrodes for Solid State Supercapacitors, Capacitive Deionization, Li-ion Battery, and Metal-Free Bifunctional Electrocatalysis

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Supporting Information

ABSTRACT: A three-dimensional nanostructured nitrogen-doped graphene/carbon nanotube composite has been synthesized via a thermal annealing process, using the high surface attachment properties of uric acid (solid nitrogen precursor) with graphene oxide and oxidized multiwalled carbon nanotube. In the synthesis procedures, the attachment of uric acid to graphene oxide surfaces and the oxidized multiwalled carbon nanotubes via hydrogen bonding and electrostatic forces in the solution leads to a lamellar nanostructure during thermal annealing by the proper insertion of carbon nanotubes in graphene layers with nitrogen doping. The resultant composite has good atomic percentage of N (11.2 at. %) and shows superior electrochemical energy storage and conversion properties compared with nitrogen-doped graphene only and physically mixed nitrogen-doped graphene and nitrogen-doped carbon nanotube samples. The composite exhibits high gravimetric and volumetric capacitance (324 F g⁻¹ at a current density of 1 A g⁻¹) as electrode in solid-state supercapacitors, superior capacitive deionization (440 F g⁻¹ at a current density of 1 A g⁻¹) in 1 M sodium chloride solution, and as high-performance anode in lithium-ion batteries (1150 mAh g⁻¹ at 0.1 A g⁻¹) with long-term cycling stability. In addition, the composite demonstrates efficient metal-free bifunctional electrocatalysis toward the oxygen reduction and evolution reactions, comparable with the commercial electrocatalysts.

KEYWORDS: nitrogen-doped graphene/carbon nanotube, supercapacitor, capacitive deionization, lithium-ion battery, metal-free bifunctional electrocatalysis

1. INTRODUCTION

The demand for high-performance energy devices, such as supercapacitors, metal–ion batteries, metal–air batteries, and fuel cells, has been growing rapidly due to the recent advances in electric vehicles and high-power-consuming portable electronics, as well as intermittent sources of renewable energy.¹,² Carbon nanomaterials have attracted great attention as potential electroactive materials for electrodes in high-performance energy devices. Their high intrinsic electrical conductivity, high charge storage capability, excellent electrochemical stability, and the low cost of environmentally friendly carbon-based nanomaterials have inspired researchers toward outstanding improvement of their performance as electroactive materials for their many real world applications.³–⁵ Most forms of carbon used commercially are limited, however, by their low capacitance, conductivity, and porosity.⁵ Even though the

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commercial carbon blacks (Vulcan carbon and Black pearls) are highly porous and conductive, they are not electrocatalytically active. Among the different forms of carbon, hexagonal graphitic carbon structures such as graphene and carbon nanotubes (CNTs) exhibit superior mechanical properties along with very high theoretical electroactive surface areas, which can provide promising electrochemical responses toward electrode materials in power devices. The strong van der Waals interactions promote restacking of graphene layers, however, which reduces the specific surface area of the active materials that offer access to the electrolyte ions, leading to an inferior electrochemical response compared to the theoretical value. Tremendous efforts are ongoing to improve the practical surface area capacity of graphene by mimicking this two-dimensional (2D) material in three-dimensional (3D) structures, as well as enhancing the electrochemical activity of individual layers by chemical modification. Alternatively, graphene-based nanocomposites with different carbon nanomaterials, conductive polymers, and metallic nanoparticles have proved to be hugely attractive because they enhance the electrical conductivity together with the surface area by preventing the restacking of graphene sheets with the aid of conjugated nanomaterials. The 3D combination of 1D carbon nanotubes with 2D graphene sheets was particularly promising because the CNTs were easily intercalated between the graphene layers. The natural inclusion and homogeneous distribution of nanotubes in the 3D structure of graphene create a highly porous composite with a very effective continuous ion-conductive network, allowing complete access by the electrolyte ions and resulting in excellent electrochemical characteristics, such as high gravimetric and volumetric capacitance, capacitive deionization and efficient electrocatalytic activity.

To obtain such a multidimensional graphitic architecture with hollow space for smooth penetration of electrolyte ions, the catalytic growth of CNTs on individual graphene layers via the chemical vapor deposition (CVD) method was explored. The results reveal the good electromechanical behavior of these promising electroactive carbon nanocomposite materials for energy devices, as well as their promising electrocatalytic activity after the insertion of metal centers. Nevertheless, because of the complicated nature of the CVD process, it is hard to scale up for large-scale production, and the presence of a metal catalyst in the process can cause detrimental effects. The formation of chemical bonding between graphene and carbon nanotubes can be an alternative way to build a three-dimensional structure for better ion interactions. Composites of reduced graphene oxide with multiwalled carbon nanotubes (MWCNTs) bonded by phenylendiamine showed good capacitive behavior, although the presence of this organic compound between the layers might degrade their electrochemical properties. The structure of the hybrid materials also suffered from problems with the insertion of carbon nanotubes inside the graphene layers. The carbon-nanotube-bridged graphene 3D building blocks, electrostatically self-assembled with cetyltrimethylammonium bromide (CTAB), showed excellent intercalation of CNTs inside the graphene layers, but the capacitance was not high enough, as the charge storage capability of reduced graphene oxide is low. The chemically bonded graphene/CNTs obtained by the amidation reaction of amine-functionalized CNTs with N-hydroxysuccinimide (NHS)-activated graphene oxide (GO) nanosheets followed by microwave hydrothermal reduction with hydrazine-ammonia showed good gravimetric as well as good volumetric capacitance as an effect of the interlayer space created by graphene. These multistep synthesis approaches, depending on highly toxic and dangerously unstable chemicals such as hydrazine, have raised the issues of facile scalable preparation of such composite materials. Besides the structural effects of graphene/CNT composites, their intrinsic capacitance, electrocatalytic responses, and continuous electrochemical stability can be improved by heteroatom doping (S, N, B, and P) in the graphene lattice, which can enhance their electronic properties based on the bonding configurations of the doped atoms with the adjacent carbon atoms. The high-temperature synthesis and nitrogen doping favors to improve electrochemical behavior by modulating of the planar electron spin density of the native carbon lattice and thus enhance the conductivity and long-term cycling stability of the electrode materials for supercapacitors and Li-ion batteries related applications. The uniformly dispersed and covalently bonded nitrogen groups on the graphene planes not only tailor the native electric double layer capacitance (EDLC) of graphene by generating pseudocapitive behavior on the edges but also provide active sites for electrocatalytic activity, such as toward the oxygen reduction reaction (ORR) via activation of the adjacent carbon atoms. In addition, the electron-dense active sites on the graphene surface are able to facilitate the oxygen evolution reaction (OER), which is a highly important characteristic for developing metal–air batteries, water splitting and fuel cells. To obtain the best performance in energy storage and electrocatalysis, the single-step scalable synthesis of a three-dimensional graphene/carbon nanotube composite with a high atomic percentage of nitrogen doping is highly desirable for electrode fabrication for high-performance energy devices. The recent approaches of facile synthesis of nanostructured N-Gr/CNT electrode materials from nitrogen-containing carbonaceous compound via thermal annealing showed superior performance in lithium–sulfur battery and electrocatalysis. However, both composites contain iron impurities coming from the precursors, which have adverse effects for capacitance, long charge–discharge cycle life, and metal-free electrocatalysis.

In this study, we have developed a scalable facile synthesis approach to nitrogen-doped graphene/carbon nanotube (N-Gr/CNT) composite material with a nanostructured lamellar architecture. The thermal annealing treatment at 800 °C under argon atmosphere of graphene oxide and oxidized carbon nanotubes combined with the solid doping precursor uric acid (UA) results in a good atomic percentage of N (11.2 at. %) in the graphitic carbon network. During the thermal treatment process at lower temperature, the doping agent UA is able to form electrostatic and hydrogen bonds with the carboxylic groups of GO and oxidized multiwalled carbon nanotube (o-MWCNT) surfaces and on the edges by its existing amino functional groups, which promotes the formation of a lamellar-structured 3D building block architecture. Under higher-temperature treatment, the solid doping precursor decomposes into highly active nitrogen species, which are homogeneously inserted into the hexagonal carbon lattice of graphene and CNTs. The appropriate intercalation of CNT networks in between the graphene layers prevents self-agglomeration and increases the mass density, as well as promoting volumetric charge storage capability. On the other hand, the nitrogen doping leads to a large number of active sites on the 3D...
network, which should make the composite suitable for high-performance metal-free electrocatalytic activity. The N-Gr/CNT performed well as electrode for solid-state supercapacitors, capacitive deionization, and Li-ion batteries. Alternatively, the bifunctional ORR and OER electrocatalytic performances of the composite were explored and it showed efficient metal-free electrocatalytic properties comparable to those of noble metal catalysts for application in metal–air batteries and fuel cells.

2. EXPERIMENTAL SECTION

2.1. Synthesis of N-Graphene. The graphene oxide (GO) was manufactured from commercially available natural graphite (Ashbury Carbons) following the previously reported synthesis method for the production of GO sheets.41 The GO nanosheets were dispersed in isopropanol using ultrasonicator. GO and the solid nitrogen precursor (uric acid) were mixed in a ratio of 1:3. The uric acid became strongly attached to the surfaces of graphene oxide due to its high adhesion properties toward organic functional groups. The mixture was then stirred with magnetic stirrer and heated at 80 °C to evaporate the isopropanol (IPA). The resulting solid powders were annealed at 800 °C at a rate of 5 °C/min for 1 h in an argon atmosphere in a tubular furnace.42

2.2. Synthesis of N-Carbon Nanotube. The oxidized multiwalled carbon nanotube (o-MWCNT) was produced by gas–solid route.43 The nitrogen doping was carried out in a similar way, using uric acid in a ratio of 1:3 via thermal annealing at 800 °C for 1 h.42

Synthesis of N-Doped Graphene/Carbon Nanotube Composites. The synthesis of N-doped graphene/carbon nanotube composites proceeded in a similar way to that stated above for the production of N-graphene. The GO, multiwalled oxidized carbon nanotube (o-MWCNT), and uric acid were mixed in a ratio of 1:3:12, respectively, in IPA solution. The mixture was then stirred with a magnetic stirrer and heated at 80 °C to evaporate the isopropanol. The resulting solid powders were then annealed at 800 °C, with heating at the rate of 5 °C/min for 1 h in argon atmosphere in a tubular furnace. The synthesized nitrogen(d)-doped reduced graphene oxide and carbon nanotube (CNT) composite was denoted as N-Gr/CNT. Physically mixed nitrogen doped graphene and N-doped CNT (with the sample denoted as PM-NGr/NCNT) was prepared by the physical mixing of NGr and NCNT in a ratio of 1:3. The mixing was done by dispersing NGr and NCNT in isopropanol and mix together using magnetic stirrer for 1 h. The mixture was then filtered by vacuum filtration and dried in room temperature to obtain the solid sample.

2.3. Characterization. The microstructure and surface morphology of the nanocomposites were studied by scanning electron microscopy (SEM; Zeiss ULTRA plus), transmission electron microscopy (TEM; JEOL 2200FS), and X-ray diffraction (XRD; Shimadzu 8600). Raman spectra were collected with a Renishaw inVia Raman Spectrometer. X-ray photoelectron spectroscopy (XPS) analysis were carried out on an ESCALAB250Xi (Thermo Scientific, U.K.) with monochromated Al Kα radiation. The XAS experiments were carried out at the wiggen XAS beamline at the Australian Synchrotron, Victoria, Australia. All the samples were stored at room temperature without special protection procedures.

2.4. Electrochemical Measurements. The electrochemical characterization and measurement of the N-doped graphene, N-doped carbon nanotube, PM-NGr/NCNT, and N-Gr/CNT were evaluated using a Biologic SP300 potentiostat by first depositing the material on an indium tin oxide (ITO)-coated glass electrode in a three-electrode cell using counter electrode of platinum wire and a reference electrode of Ag/AgCl, KCl (3 M). The N-Gr/CNT composite samples were manufactured by mixing 1 mg/mL of the material in isopropanol using sonication. For characterizing the capacitance properties, 10 wt % polytetrafluoroethylene (PTFE) was used as binding agent. For the capacitance calculations, a two-electrode cell was developed using ITO-coated glass electrodes. The device was fabricated by depositing the active materials on the conductive side of the ITO-coated glass and inserting a separator designed for aqueous electrolyte (Celgard) between the coated electrodes, which were pressed together at high pressure. Before the device was fabricated, the separator was soaked in electrolyte (0.5 M sulfuric acid) for 1 h. Next, 0.5 g of active materials was deposited over the area of 2.0 cm × 2.0 cm on an ITO-coated glass electrode surface using 10 wt % PTFE binder. The solid-state device was fabricated in a similar way, replacing the separator soaked in electrolyte by a gel electrolyte composed of poly(vinyl alcohol)/sulfuric acid. The preparation of the gel electrolyte followed the reported procedure.42 First, 2.2 g of poly(vinyl alcohol) (PVA) powder was added into 20 mL of water and then heated to around 90 °C. Continuous stirring until the solution becomes clear. Then, 2.2 g of sulfuric acid was added, and the solution was cooled down to room temperature to form the gel electrolyte. The solid state supercapacitor was fabricated by depositing the active material on both of the ITO-coated glass slides and putting them together with two glass spacers on both sides to make a gap between the two electrodes. The gap was then filled up by the gel electrolyte. The gravimetric capacitance of the cell from galvanostatic charge/discharge was calculated using the formula for capacitance measurement.42

For capacitive deionization, NGr, NCNT, PM-NGr/NCNT, and N-Gr/CNT were coated on the graphite paper with 10% PTFE binder to investigate the total electroosorption capacities. The mass of the active materials was 10 mg on each of the electrodes. The electrodes were dried at over 100 °C for 12.5 s. The capacities were measured first in 1.0 M sodium chloride solution in two-electrode cells. A two-electrode-based flow cell connected with a peristaltic pump and conductivity meter was used to measure the capacitive deionization profile. In the flow cell, aqueous solution of sodium chloride with an initial conductivity of 1030 μS cm⁻² was fed using a pump with a flow rate of 12 mL/min. The applied voltage was adjusted to 1.2 V. The change of concentration was measured by the connected conductivity meter at the outlet of the cell. The capacitive deionization behavior in actual seawater was also observed.

For the Li-ion battery, the electrochemical characterization of NGr/CNT composite was carried out using coin cells. The electrode was tape-casted over Cu foil by blending the active material, N-Gr/CNT, with Super P carbon black and polyvinylidene difluoride (PVDF) binder, in a weight ratio of 8:1:1, respectively using N-methyl-2-pyrrolidone (NMP) as the blending solvent and subsequently drying the electrode at 120 °C for 12 h. The electrode was then cut into circular discs with controlled mass loading of ~1 mg cm⁻². CR 2032 coin-type cells were assembled in an Ar-filled glovebox (MBraun, Germany), and the as-prepared electrodes were then used as the working electrode, with Li foil as the counter electrode/reference electrode, a porous Celgard film as separator, and 1 M LiPF₆ in a 1:1 (v/v) mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) as the electrolyte. The cells were galvanostatically charged and discharged using an automatic battery tester system (Land, China) at various current densities in the range of 0.002–3 V. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements were performed (Bio-Logic, Science Instruments, Model: VMP-3) at 0.2 mV s⁻¹ between 0.0398 V and 0.1 MHz with 5 mV amplitude. The specific capacity of the assembled Li-ion battery was calculated based on the mass of active material, N-Gr/CNT, neglecting the effect of Super P carbon black due to its low reversible capacity.

The electrocatalytic properties of the samples were assessed by RDE (rotating disk electrode) in 0.1 M KOH solution saturated with oxygen. Initially, the electrocatalytic property for oxygen reduction reaction was determined by comparing the CVs observed in argon saturated and oxygen saturated electrolytes. The LSV (Linear sweep voltammetry) curves were obtained at the potential limit of 0 to 1 V versus RHE at 10 mV s⁻¹ scan rate at rotation speeds of 100–1600 rpm. The active materials were dispersed in isopropanol solution at a concentration of 1 mg mL⁻¹ with 5 wt % nafion as a binder. The surface area of glassy carbon electrode (GCE) was equal to 0.196 cm². The weight of the electrodes on the GCE for testing electrocatalysis
were evaluated by depositing 12 μg of active materials that equal to 0.061 mg cm⁻² of catalyst loading on the substrate surface. OER activity was determined by LSV in the potential window ranging from 1.0 to 2.0 V versus RHE. The Pt/C and Ru/C electrodes are prepared by commercial purchased Pt/C (20 wt %) and Ru/C (20 wt %) in Nafion solution with same loading amount were used for comparison.

3. RESULTS AND DISCUSSION

The synthesis of N-Gr/CNT is illustrated in Figure 1, where the graphene oxide (GO), oxidized carbon nanotubes (o-CNT), and uric acid (UA) are mixed together in isopropanol in the ratio of 1:3:12, respectively, and stirred continuously at a temperature of 80 °C until the complete evaporation of solvent. The uric acid molecules adsorbed strongly via hydrogen bonding on the carboxyl groups on the graphene oxide and the o-CNT surfaces, forming a lamellar structure via intercalating the o-CNTs in graphene layers. The solid mixture was collected in powder form and then annealed in the furnace at 800 °C at a ramp of 5 °C/min for 1 h.

During pyrolysis, inclusion in the graphene lattice of nitrogen atoms from the uric acid occurs and a lamellar structure is formed, composed of nitrogen-doped graphene/carbon nanotube composite containing a high atomic percentage of nitrogen. The attachment to the graphene oxide of the oxidized carbon nanotube took place through the formation of hydrogen bonding between the amino groups of uric acid (UA) and the carboxylic groups of GO and o-CNT. Uric acid, because of its good adhesive properties, can form hydrogen bonds with carboxyl groups with an adhesion force of 1.62 nN.⁴³ During the sonication and stirring at 80 °C, because of its excellent surface attachment properties, the uric acid can be intercalated inside the graphene layers, interconnecting the graphene layers and o-CNTs by forming hydrogen bonds with the carboxyl groups. The Fourier transform infrared (FTIR) spectra (Figure 2) show a comparison of the UA, the binary mixture of graphene oxide with oxidized carbon nanotube (GO/o-CNT), and the ternary composition of (GO/UA/o-CNT). The GO/UA/o-CNT mixture was filtered and washed several times to remove the excess uric acid from the GO/o-CNT surfaces. The uric acid shows its characteristic FTIR spectrum. The absorption bands of the GO/o-CNT mixture appear at 3200−3600 (broad peak), 1726, 1640, 1582, 1226, 1160, and 1125 cm⁻¹, which correspond to −OH and C==O in carboxyl groups, C==C aromatic rings, and C−OH, C==O, and C−O stretching vibrations, respectively. In the spectra of GO/UA/o-CNT, the presence of uric acid was observed due to its strong signal toward the IR region, which did not appear with the GO/CNT mixture. Small shifts toward the left of C==O stretching (1658 cm⁻¹) and N−O stretching (1585 cm⁻¹) could be observed in GO/UA/o-CNT from the C==O stretching (1664 cm⁻¹) and N−O stretching (1589 cm⁻¹) of uric acid, indicating the formation of hydrogen bonding.⁴⁴

The morphology and structure of the obtained composite after pyrolysis were characterized by SEM and TEM. The SEM images of N-Gr/CNT revealed the intercalated CNT networks inside the graphene layers (Figure 3a and Figure S1). The three-dimensional structure and the intercalation of carbon nanotubes inside the graphene layers are clearly visible. For further confirmation, low-magnification TEM was used. The TEM image confirms the 3D structure of the composite, created by forming CNT networks inside the graphene layers.

Figure 2. FTIR spectra of uric acid; the mixture of graphene oxide with oxidized carbon nanotubes; and the mixture of graphene oxide, oxidized carbon nanotube, and uric acid.

Figure 3. (a) SEM image of three-dimensional nanostructured N-Gr/CNT, (b) SEM image of PM-NG/NCNT, (c) TEM image of N-Gr/CNT, (d) TEM image of PM-NG/NCNT.
(Figure 3c). In contrast, in the physically mixed nitrogen-doped graphene and nitrogen-doped carbon nanotube (PM-NGr/NCNT), the CNTs are randomly situated on the graphene surface (Figure 3b), and similar morphology was found in the TEM image (Figure 3d).

High-resolution TEM (HRTEM) revealed the attachment of CNTs on the edges as well as the basal planes of the graphene (Figure 4a). The average d-spacing of the graphene layers of graphene-like structure due to the random agglomeration of graphene sheets and carbon nanotubes.

Energy dispersive X-ray spectroscopy (EDS) with SEM was applied to characterize the doped regions and elemental distribution of carbon along with nitrogen in the hybrid N-Gr/ CNT (Figure S2). From the EDS mapping, it can be observed that the carbon and nitrogen atoms are well-distributed throughout the surface, and the presence of a high percentage of nitrogen over all the surface is found. The elemental composition and nitrogen content in the composites were evaluated by XPS. From the XPS measurements of N-Gr/CNT and PM-NGr/NCNT, the survey spectra of both of the composites confirm the existence of C, O, and N. In Figure 5a,

![Graph showing Raman spectra](image)

Figure 4. (a) HRTEM image of N-Gr/CNT with selected area (indicated by arrow) for calculating d-spacing. (b) d-spacing calculation. (c) XRD patterns of N-Gr/CNT (i), PM-NGr/NCNT (ii), NGr (iii), and NCNT (iv). (d) Raman spectra of N-Gr/CNT and PM-NGr/NCNT.

N-Gr/CNT from HRTEM was found to be 0.3946 nm (Figure 4b), which is larger than the average layer-to-layer spacing of 0.352 nm observed in thermally reduced graphene oxide film. The increase in the spacing between the graphene layers was expected due to the presence of CNTs at the edges to prevent restacking between the layers. The spacing between the layers of graphene was also characterized by XRD (Figure 4c). Evaluation of the peak positions indicated a slight shifting of the peaks of the composites compared to the peaks for NG and NCNT. The calculated interlayer spacing found from the peak position was 0.38 nm, which is higher than the average layer-to-layer spacing of graphene and close to the value obtained from HRTEM. The broader peak of N-Gr/CNT also indicates the formation of uneven surface structure and orientation due to the intercalation of CNTs inside the graphene layers. The graphic nature and carbon lattice defects resulting from the doping effects in both the N-Gr/CNT and the PM-NGr/NCNT composites were evaluated by Raman spectroscopy at an excitation wavelength of 514 nm. In Figure 4d, the G peaks of N-Gr/CNT and PM-NGr/NCNT were present at 1578 and 1582 cm⁻¹, respectively. The position of the G peak of N-Gr/CNT was shifted toward the left, as shown reducing intensity compared with the G peak of PM-NGr/NCNT, which indicates the presence of more defects due to the combined nitrogen doping rather than separate doping and physical mixing.

![Graph showing XPS spectra](image)

Figure 5. (a) XPS survey spectra of N-Gr/CNT and PM-NGr/NCNT. (b) N 1s XPS peak of N-Gr/CNT. (c) Cyclic voltammograms of (i) NCNT, (ii) NGr, (iii) PM-NGr/NCNT, and (iv) N-Gr/CNT, in the three-electrode cell at 100 mV s⁻¹ scan rate. (d) Cyclic voltammograms of N-Gr/CNT at different scan rates: (i) 50, (ii) 100, and (iii) 200 mV s⁻¹.

Distinctive 2D peaks of N-Gr/CNT were observed at 2688 and 2722 cm⁻¹, which confirmed the state of the composites as lamellar few-layers graphene flakes, whereas the broad 2D peak of PM-NGr/NCNT resembled a multilayered for both of the composites, the high-resolution C 1s peak is centered at 284.4 eV. It has a tail at higher binding energies, indicating the connection of carbon atoms with N and O heteroatoms. The peak deconvolution of N 1s shows (Figure 5b) five possible nitrogen configurations in N-Gr/CNT. These include 46.0% pyridinic N (N1, N in 6-member ring), 14.4% pyrrolic N (N2, N in 5-member ring), 31.0% graphitic N (N3, N in graphene basal plane), 6.2% oxidized N (N4, N−O), and 2.4% protonated N (N5, N−H), with a total nitrogen content of 11.21%. The N 1s peak deconvolution of PM-NGr/NCNT shows 46.4% pyridinic N, 13.6% pyrrolic N, 28.5% graphitic N, 9.3% oxidized N, and 2.2% protonated N (N5, N−H) (Figure S3), with a total nitrogen content of 6.9%. The atomic percentage of nitrogen was higher in N-Gr/CNT, possibly due to the better interaction with the dopant during the one-pot mixing before pyrolysis. The high-resolution C 1s XPS spectrum can be deconvoluted as four peaks at 284.5, 285.0, 286.6, and 288.0 eV for C−C, C=O, C−N, and O−C=O, respectively, for N-Gr/CNT (Figure S4a) and PM-NGr/CNT (Figure S4b). Both of the samples contained similar carbon configurations; however, N-Gr/CNT has comparatively less C−C bond and high C=O bond and C=N bond due to the higher amount of nitrogen doping.

To further explore the types of carbon—carbon and carbon—nitrogen bond formations, the XAS (X-ray absorption
spectroscopy) analysis has been performed. X-ray absorption spectroscopy is a powerful probe of the electronic structure to excite core electrons into unoccupied bound or continuum states with the tunable X-ray source. The C K-edge XANES spectrum (Figure S5) exhibits the features of typical sp2 coordinated carbon atoms in a good agreement of multilayer graphene, such as the sharp peak around 285.2 eV and the excitation peak of $\sigma^*$ at 291.9 eV for all the four samples of reduced graphene oxide, nitrogen-doped graphene, PM-NGr/NCNT and N-Gr/CNT. The nitrogenation significantly changes the spectral features and line shapes of the three nitrogen-doped composite compared to reduced graphene oxide. All the materials showed peaks at $\sim$285.4 eV (C=C bond). The peak at $\sim$286.5 that is only observed for N-Gr/CNT was assigned to $\pi^*$ excitation for carbon for [1 s $\rightarrow$ $\pi^*$ ($\varepsilon_{2g}$)] transition identical to that of pyridine (C=N). The peaks at $\sim$287.2, $\sim$288.5, and $\sim$289.2 eV are for $\pi^*$ C-H/C- OH, $\pi^*$ C-OH/C=O, and C-N bond with the carbonyl functionality nearby, respectively. The N K-edge XANES spectra of nitrogen-doped graphene composites (Figure S6) provide evidence of the local electronic states that are bound to the nitrogen sites. In the $\pi^*$ region, a strong feature (N2) of high intensity at $\sim$400.2 eV is assigned to the C-N= triplet in N-Gr/CNT compared to NGr and PM-NGr/NCNT. At $\sim$399.2 eV and at $\sim$401.5 eV are attributed to the pyridinic/pyrrolic N-related group with two carbon neighbors in six-/five-membered ring. In the $\pi^*$-region, the 1 s $\rightarrow$ $\pi^*$ transition at $\sim$406.4 eV is associated with the superposition of graphite-like and pyridine-like nitrogen structures, and the intensity decreases with the atomic percentage of nitrogen. The Brunauer–Emmett–Teller (BET) surface areas of both the composites were measured (Figure S7), and a higher surface area was observed for N-Gr/CNT (293 m$^2$ g$^{-1}$) than for PM-NGr/NCNT (210 m$^2$ g$^{-1}$). The surface areas higher than the surface area measured for NGr (198 m$^2$ g$^{-1}$) synthesized via a similar method. The total pore volume of N-Gr/CNT was found to be 0.55 cm$^3$ g$^{-1}$, the micropore volume was 0.035 cm$^3$ g$^{-1}$, and the average pore width was 7.4 nm.

3.1. Electrochemical Properties of N-Gr/CNT for Supercapacitors. Cyclic voltammetry (CV) was used to study the electrochemical behavior of NG, NCNT, N-Gr/CNT, and PM-NGr/NCNT deposited on ITO-coated glass electrodes in 0.5 M aqueous H$_2$SO$_4$ electrolyte (Figure 5c). PTFE solution of 10 wt% was applied as binding agent. From the CVs, it was observed that the CV of NCNT showed the lowest capacitive response due to the characteristic low capacitance of multiwalled carbon nanotube. The NGr showed better capacitive behavior than the NCNT due to the contribution of electrochemical double layer capacitance along with the pseudo capacitance originating from the N-doped active sites on the graphene surface and the increased surface area due to the high temperature doping. Interestingly, the capacitive response of PM-NGr/CNT was slightly lower than that of NGr, even though it was expected to show some increased capacitance due to its relatively higher surface area than NGr. The possible reason for this relatively low capacitance of PM-NGr/NCNT is the lack of three-dimensional structure, as well as the low capacitive response of NCNT, which affects the overall capacitance properties of the composite.

The CV of N-Gr/CNT showed the highest capacitive response, with its electrochemical double layer capacitance indicating better penetration of electrolyte ions inside the lamellar structure of the composite. The interlayer spacing (as evidenced by XRD) was due to the intercalation of CNTs on the edges between the graphene layers, providing room for the electrolyte to penetrate through the composite and yield the maximum capacitive responses from both sides of the graphene layers. The CV curves of N-Gr/CNT at different scan rates of 50, 100, and 200 mV s$^{-1}$ had been observed (Figure 5d). To reveal the capacitive properties of N-Gr/CNT for practical application, a two-electrode symmetric supercapacitor cell based on ITO-coated glass current collectors with an area of 1 cm$^2$ (1 cm $\times$ 1 cm) was constructed. As presented in Figure 6a,b, the active material was drop-casted on the conductive sides of the current collectors by dispersing the composite material in isopropanol solution with PTFE binder and drying the resultant electrodes at room temperature. The separator (Celgard) was first soaked in the aqueous electrolyte solution for 1 h, and then the two electrodes were sandwiched together under pressure with the separator inserted between them. CVs of the cell at three different scan rates of 50, 100, and 200 mV s$^{-1}$, indicated almost rectangular voltammograms (Figure 6c), clearly indicating the excellent capacitive nature of the as-prepared material, even in a device application. The ideal charge storage capability of the material is also reflected in the charge–discharge (CD) profiles (Figure 6d) at different current densities (1 to 10 A g$^{-1}$). The specific capacitance ($C_p$) of the electrode material was calculated from the galvanostatic discharge profile in the CD study (Figure 6d). The $C_p$ value for N-Gr/CNT was found to be 324 F g$^{-1}$ in 0.5 M H$_2$SO$_4$, at a current density of 1 A g$^{-1}$. At a high current density of 10 A g$^{-1}$, the specific capacitance maintained as good as 220 F g$^{-1}$. After demonstrating the high capacitance property in the sandwiched two-electrode device, a solid-state two-electrode device was fabricated by the gel electrolyte, along with the replacement of the separator soaked with electrolyte (Figure S8). The fabrication of solid-state devices is highly important for the advancement of portable, wearable,
The gel electrolyte preparation was performed by mixing a heated PVA solution with 0.5 M sulfuric acid, following the reported procedure. The solid-state device (Figure S8a, S8b) was fabricated by inserting a glass spacer between the active materials deposited on the ITO-coated glass, and the empty space between the two electrodes was filled up by the gel electrolyte. The electrochemical properties of the solid-state device were explored by cyclic voltammetry, and the CV curves (Figure S8c) at high scan rates (100, 200, and 500 mV s⁻¹) showed reversible electrochemical properties with high capacitance, but only slight resistivity, which is characteristic of gel electrolytes. The galvanostatic charge–discharge curves showed distortion from the theoretical ideal charge–discharge curve due to the contributions of pseudocapacitance and the device fabrication method (Figure S8d). The specific capacitance of 312 F g⁻¹ was obtained from the discharge curve at a high current density of 1 A g⁻¹. The high capacitance of 224 F g⁻¹ was also observed at the high current density of 10 A g⁻¹. The specific capacitance of the solid-state device was slightly lower than the specific capacitance of the two-electrode devices, which may be because the solid electrolyte ions face more resistance when they penetrate the solid surface of the dry electrolyte gel material at higher current density. Even though the greater resistivity degrades the capacitance property, the replacement of the separator by gel electrolyte shortens the transport pathways of the ions, which contributes to better ion diffusion on the electrode, so that there was only a slight decrease in the capacitance. Comparison of the CV curves and charge–discharge curves also showed distortion of the gel electrolyte in the solid-state device (Figure S9). The volumetric capacitance was calculated by multiplying the electrode mass density by the gravimetric capacitance. The mass density of N-Gr/CNT was calculated from the average thickness of the mass loading on the electrode from cross-sectional SEM. The value of the mass density was found to be 0.97 g cm⁻³, which is reasonable due to the high mass loading of the active material on the electrode. This value is also comparable with that of a reported three-dimensional composite of activated graphene/single-walled carbon nanotube (1.06 g cm⁻³). The volumetric capacitance of 302 F cm⁻³ at the high current density of 1 A g⁻¹ is the highest value among the reported values for capacitance related to graphene/carbon nanotube-based supercapacitors, as well as being comparable with the values for three-dimensional structured nanocarbon-based supercapacitors (Table S1). The energy and power density of the solid-state device were calculated using the discharge rates. The highest energy density of 15.60 Wh kg⁻¹ was achieved at the power density of 702 W/kg, and the energy density of 11 Wh kg⁻¹ was retained at a high power density of 6600 W kg⁻¹. The high capacitance performance of N-Gr/CNT could be attributed to the addition of pseudocapacitance to the
electrochemical double-layer capacitance, for the elevated atomic percentage of nitrogen enriched with high ratios of pyrrolic N and graphitic N atomic states in a planar graphitic carbon framework. The high surface area, pore volume, and lamellar structure influenced to achieve superior conductivity with enhanced electrolyte penetration. The device cycling stability was first measured at the high current density of 5 A g⁻¹ over 2000 cycles between 1.0 and 0 V, and excellent capacity retention of 96% of its initial capacitance was revealed. To observe the lifetime of the solid-state cell, the cycling test was continued up to 10 000 cycles at the same current density of 5 A g⁻¹. The cell exhibited capacity retention of 82% after 5000 cycles and 46% after 10 000 cycles, which indicates its stability at very high current density, even with gel electrolyte and with laboratory grade manual fabrication (Figure S10a).

The Nyquist plots before and after cycling confirmed the high electrochemical stability of the device (Figure S10b).

3.2. Capacitive Deionization of N-Gr/CNT for Desalination. The superior capacitance properties of N-Gr/CNT led us to investigate the capacitive deionization properties of this composite. Graphene oxide, graphene, carbon nanotube, and their composites have been proven as an emerging electrode materials for capacitive deionization and desalination. The nitrogen doping into the graphitic network enhanced the conductivity, surface area, pore volume, and wettability of the interface between the electrolyte and electrodes. It helps to capture the salt ion easily by the electrode materials, thus accelerating the salt adsorption rate.

In addition, the three-dimensional nanostructure further improves the electrochemical double layer capacitance with
low internal resistance and better ion permeability. The pore size and pore volume of chemical doped and nanostructured graphene have played the important roles to enhance the electrosorption properties to capture sodium ions. To characterize the capacitive properties of the composites, cyclic voltammograms technique had been utilized to investigate the electrochemical behavior of NG, NCNT, NGr/CNT, and PM-NGr/NCNT casted on graphite paper in 1.0 M aqueous NaCl electrolyte within potential limits of −0.5 to 0.5 V in a two-electrode system at 75 mV s−1 (Figure 7a). From the CVs, it was observed that all the carbon composites showed typical rectangular capacitor-like characteristics and NGr/CNT was showing the highest amperometric signals. In the CV curves, no oxidation/reduction peaks were observed that indicated the adsorption of ions on the electrode surfaces by forming electrochemical double layer capacitances rather than electrochemical reactions. The three-dimensional nanostructures, high amount of nitrogen doping (11.2 atomic percentage), high surface area (293 m²/g), relatively higher average pore size (7.54 nm), and pore volume (0.55 cm³/g) played the key roles for electrolyte permeation and ion adsorption for NGr/CNT. The amperometric signals of the rectangular CV curves of NGr/CNT with the scan rates were observed (Figure 7b). The charge–discharge curves (Figure 7c) shows the high capacitance properties of 440 F/g at a current density of 1 A/g. This superior capacitance is due to the three-dimensional structures, high surface area, and nitrogen doping, which facilitate the adsorption of sodium ions. 26,60,61 In addition the high conductivity, defected surface and nanoporous structure enhance the electro-capacitive properties. To further evaluate the desalination properties of the three-dimensional nanostructured NGr/CNT electrode, the CDI cell in a batch-mode apparatus with a sodium chloride solution of high initial conductivity was introduced. The adsorption/desorption behaviors of the CDI electrode were evaluated by the change of conductivity of sodium chloride aqueous solution. The electrosorptive properties of NGr/CNT were investigated by continuous flow of electrolytes with high initial conductivity. Figure 7d exhibits the typical conductivity transient of NGr/CNT electrode in sodium chloride solution with an initial conductivity of 1030 µS cm⁻¹ at an applied voltage of 1.2 V. The conductivity started to decrease with the time during charging. Initially rapid decrement of conductivity was observed up to 40 min and the rate of conductivity reduction process become slow due to the saturation of ion adsorption in the nanoporous structure and plateaued after 60 min. In the capacitive deionization process, the plot of the solution conductivity of NGr/CNT did not show rapid decrease of conductivity due to the high heteroatom doping that lead to slow charge efficiency due to the parasitic faradaic reaction during salt removal process. 60 The conductivity of the solution was reduced to 980 µS cm⁻¹ after 60 min. The CDI capacitance was calculated using the following eq 1:

\[ \text{C} = \frac{(C_0 - C_s) \times V}{m} \]  

where \(C_0\) and \(C_s\) are initial and final sodium chloride concentration (mg L⁻¹), \(V\) is the volume of NaCl solution (L), and \(m\) is the mass of the electrodes in grams. The obtained value of 25.74 mg/g demonstrated the excellent electrosorption properties of NGr/CNT electrode. The high amount of doping created defects that favored the rapid ion diffusion, electrical conductivity, and wettabiility. In addition, the three-dimensional nanostructure facilitated the ion permeability and high surface area as well as high capacitive ion storage properties of the composite. The electrochemical capacitance behavior of the electrode in 1 M NaCl electrolyte was compared with seawater electrolyte (Figure S11), and it showed a similar amperometric signal with a rectangular CV curve that indicates a possible real-life application for desalination of seawater.

3.3. Electrochemical Performance of N-Gr/CNT as Anode for the Li-Ion Battery. Three-dimensional porous carbon structures have been shown to be excellent anode materials in metal–ion batteries. 62,63,64 The incorporation of nitrogen in the three-dimensional structure can increase the Li-ion storage capacity, facilitate Li-ion adsorption, enhance ion diffusion through the structural defects, and increase the cycling stability. 65,66 After observing the superior capacitance performance, we explored the electrochemical properties of NGr/CNT as anode for the Li-ion battery, as this material enriched with lamellar structure possesses a high surface area with efficient pore size and a decent atomic percentage of nitrogen. The cyclic voltammograms from 0.002 to 3 V exhibit the activity of the composite in lithium-ion batteries and correspond to the charge–discharge curves. As can be seen from Figure 8a, the first cathodic peak centered at 0.56 V corresponds to the formation of a dense solid electrolyte interphase (SEI) layer over the electrode’s surface due to electrolyte decomposition, and this peak vanishes in the subsequent cycles. The second cathodic peak centered around 1.34 V corresponds to the Li⁺ insertion into the composite, which is an important indication of lithium storage in NGr/CNT. The CV curves were quite similar after the second cycle, indicating that a stable state had been achieved. The capacity above 0.5 V is associated with defects, the 3D architecture and layers, pores, and Li binding with heteroatoms. 62,63,64 During the Li removal/charging process, the potential hysteresis indicated the removal of inserted lithium ions within a wide potential range of 0.1 to 3 V, with the associated peaks at 0.2 and 1.2 V representing lithium extraction from the graphene layers and pore structures/defects, respectively. 65 The composite was subjected to rate capability testing at various current densities and to long-term cycling stability testing at 0.5 and 1 A g⁻¹. When cycled at various current densities from 0.1 to 10 A g⁻¹ (Figure 8c), the composite exhibited reversible capacities of 1150, 500, 350, 300, 250, and 200 mA h g⁻¹ at 0.1, 0.5, 1, 3, 5, and 10 A g⁻¹ (60 cycles), respectively. After cycling at various rates, the specific capacity could still be recovered to 1150 mA h g⁻¹, implying high stability and reversibility. The specific capacitance of 1150 mA h g⁻¹ obtained at 0.1 A g⁻¹ is 3 times greater compared to the theoretical capacity of graphite (372 mA h g⁻¹) and is the highest capacity that has been reported so far for metal-free N-doped graphene and N-doped graphene/carbon nanotube based anode materials (Table S1).

Very good cycling stability with reversible battery capacity of 1150, 400, and 350 mA h g⁻¹ was observed at current densities of 0.1, 0.5, and 1 A g⁻¹ with a first cycle initial Coulombic efficiency of 73.8%, 65.7% and 60.1% respectively. The initial capacity loss are intrinsic property of high-surface-area carbonaceous materials owing to the formation of irreversible solid electrolyte interface (SEI), but this could be mitigated by preforming of SEI layer before cell making so as to obtain stable and long cycle life. 27 A rapid increase in the capacity was observed at the high current densities of 0.5 and 1 A g⁻¹, as shown in Figure 8d. This initial low performance may be
due to trapping of Li\(^+\) ions in the SEI layer, which then fractures, leading to reactivation of the lamellar structure. The heavily nitrogen-doped active material eases the ion diffusion through its porous structure created by the defects, so that it efficiently recovers the large initial loss of capacity and enhances the lithium storage performance at high rates.

To test the long-term cycling stability, the cell was operated for up to 1250 cycles at a high current density of 1 A g\(^-1\) (Figure 8e) and demonstrated its superb stability for commercial application. Under long cycling at high current density, the three-dimensional structure was expanded to create space for ion storage, and the capacitance kept increasing. After a long cycle life of 900 cycles at high current density, the structure started to become distorted, and fluctuations in the capacity were observed possibly due to the incorporation of high extent of lithium ion into the electrodes that blocked the pores and reduced the capacitance properties. The Nyquist plots in Figure 8d of the fresh material and after 1250 cycles can enable us to better understand the reasons for the excellent cycling stability of the N-Gr/CNT composite. The EIS plot after 1250 cycles possesses a depressed semicircle and a smaller interfacial charge-transfer resistance, demonstrating the good electronic conductivity of the composite, which enhances the Li\(^+\) ion transport across the interface between the electrolyte and the active materials. Initially, the conductivity of the cell was not sufficient, but after cycling, the electrolyte achieved better permeation in the three-dimensional nanostructured material. The expansion of the graphene layers also provided the space to store more charge, which led to enhanced conductivity and capacity. The EIS spectrum after 500 cycles demonstrated the high conductivity of the composite. After 1250 cycles, the conductivity decreased compared with after 500 cycles, but it was still higher than in the initial state. The lamellar structure with the heavily nitrogen-doped active material eases ion diffusion through its porous structure created by the defects and efficiently recovers the large initial loss of capacity, leading to enhanced lithium storage performance storage at high rates.

3.4. Electrocatalytic Activity of N-Gr/CNT as Bifunctional Electro catalyst for the ORR and OER. N-Gr/CNT was explored as a bifunctional electrocatalyst for the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER). The active electrodes were deposited on GCE (~12 \(\mu\)g mass loading) and its electrocatalytic activity and those of the related materials NGr, NCNT, and PM-NGr/NCNT were investigated using rotating disk electrodes (RDE). Figure 9a shows the linear sweep voltammograms (LSVs) of NGr, NCNT, PM-NGr/NCNT, N-Gr/CNT, and Pt/C, all measured at 10 mV s\(^{-1}\) with rotation speed of 1600 rpm in electrolyte saturated with oxygen of 0.1-M KOH. The N-Gr/CNT produced the most positive onset potential of +0.8 V at −0.5 mA cm\(^{-2}\) and highest current density of −4.7 mA cm\(^{-2}\) among the synthesized NGr, NCNT, and PM-NGr/NCNT samples, and they were close to those of Pt/C. The LSV curves (Figure 9b) at different rotation speeds were used to calculate the number of electrons transferred to an oxygen molecule via the Koutecky–Levich equation.\(^{12,74}\)

The N-Gr/CNT electrode showed linearity (coefficient of determination, \(R^2 = 0.998\)) in the Koutecky–Levich plot of \(j_\text{app} vs \omega^{-1/2}\) at a potential of 0.6 V. The average electron transfer number was 3.94 at different potentials of 0.6, 0.5, 0.4, and 0.3 V (Figure S12a) at the current densities of 3, 3.75, 4.1, and 4.4

Figure 9. (a) LSV of NCNT, NGr, PM-NGr/NCNT, N-Gr/CNT, and Pt/C at a scan rate of 10 mV s\(^{-1}\) with 1600 rpm in 0.1-M KOH(aq) saturated with oxygen. (b) RDE measurements of N-Gr/CNT. (c) LSV of N-Gr/CNT, PM-NGr/NCNT, Ru/C, and Pt/C at a scan rate of 10 mV/s in 0.1-M KOH(aq). (d) LSV curves of N-Gr/CNT and Pt/C on an RDE (1600 rpm).
mA cm⁻², respectively, which confirms the four-electron process.

To further investigate the potential application of three-dimensional metal-free nanostructured N-Gr/CNT, the electrocatalytic activity toward the OER was evaluated by conducting the LSV at a potential range of 1.0 to 2.0 V. The onset potentials were measured at 1.48, 1.50, 1.46, and 1.68 V for N-Gr/CNT, PM-NGr/NCNT, Ru/C, and Pt/C, respectively (Figure 9c), from the LSV curves. The potentials to achieve the current density of 10 mA cm⁻² were assessed as 1.65, 1.76, 1.64, and 1.88 V for N-Gr/CNT, PM-NGr/NCNT, Ru/C, and Pt/C, respectively. Therefore, N-Gr/CNT showed the least onset potential and largest current density in comparison with PM-NGr/NCNT and Pt/C, as well as being almost the same as for Ru/C.⁷⁵ The Tafel slopes for the N-Gr/CNT, Ru/C, and Pt/C were about 126, 109, and 238 mV/decade, respectively, so that the slope for N-Gr/CNT was much smaller than for Pt/C (238 mV/decade) and slightly larger than for Ru/C, which indicated the superior OER activity of N-Gr/CNT (Figure S12b). The OER performance of N-Gr/CNT was superior compared with the Pt/C and comparable to those of the metal-based electrocatalysts, metal-free three-dimensional carbon nanostructures,¹⁸ and dual-doped carbon.⁷⁹

Since the OER activity in chemical-doped graphene is highly dependent on the structure and atomic weight percentages of dopants,⁷⁵,⁷⁸–⁸⁰ the high OER activity in N-Gr/CNT may be due to the three-dimensional nanostructure. Other factors include the existence of a large at.% of nitrogen and the high surface area with pore volume. The three-dimensional nanostructure with CNTs on the edges of graphene layers and high percentages of pyridinic N and graphitic N on the edges of the graphene sheets creates the active sites needed for efficient bimetallic reactions toward oxygen reduction and evolution. In comparison with the bifunctional electrocatalytic performance of our samples with the performance of Pt/C, measured by LSV plots at 1600 rpm in oxygen-saturated 0.1 M KOH (Figure 9d), a comparable ORR with a four-electron transfer pathway and better OER activity of the N-Gr/CNT were identified. From the ORR activity, the onset potential and current density of N-Gr/CNT were lesser than the Pt/C. The excellent electrocatalytic behavior of lower onset potential and higher current density compared with Pt/C and closer to the performance of Ru/C for N-Gr/CNT in OER were observed. This bifunctional electrocatalytic properties with the remarkable charge storage properties can make this three-dimensional nanostructured electrode an alternative candidate for developing metal–air batteries and reversible fuel cells.

4. CONCLUSIONS

In conclusion, a facile synthesis method for a three-dimensional lamellar-structured, nitrogen-doped graphene/carbon nanotube hybrid, featuring high surface area as well as high atomic percentage of nitrogen is reported. The synthesized N-Gr/CNT showed excellent capacitive properties when incorporated in a solid-state supercapacitor device, efficient capacitive deionization properties, high rate capability as anode for the lithium-ion battery, and metal-free bifunctional electrocatalytic performance toward the ORR and OER. These multifunctional properties could lead to the development of hybrid energy-storage and conversion devices, high-performance metal–oxygen energy storage and reversible fuel cells. The tuning of three-dimensional structure by incorporating nanostructured metal particles, conductive polymers, 2D layered materials, and nanocarbons could further improve its application in a wide range electrochemical applications.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsaeem.8b00845.

SEM images, XPS analysis, XAS analysis, BET, electrochemical capacitive behavior, stability test and EIS, comparison of capacitive deionization properties in 1 M NaCl and sea water, Rourke-Levich plot for ORR, and comparison table with the state-of-the-art electrodes (PDF)

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Notes
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