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Manganese dioxide-anchored three-dimensional nitrogen-doped graphene hybrid aerogels as excellent anode materials for lithium ion batteries

Abstract

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Keywords

materials, anode, excellent, aerogels, hybrid, graphene, doped, nitrogen, dimensional, lithium, three, manganese, ion, batteries, anchored, dioxide

Disciplines

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Abstract

The capacity of manganese dioxide (MnO_2) deteriorates with cycling due to the irreversible changes induced by the repeated lithiation and delithiation processes. To overcome this drawback, MnO_2 /nitrogen-doped graphene hybrid aerogels (MNGAs) were prepared via a facile redox process between KMnO_4 and carbon within nitrogen-doped graphene hydrogels. The three-dimensional nitrogen-doped graphene hydrogels were prepared and utilized as matrices for MnO_2 deposition. The MNGAs-120 obtained after a deposition time of 120 min delivered a very high discharge capacity of 909 mA h g^{-1} after 200 cycles at a current density of 400 mA g^{-1} , in sharp contrast to only 280 and 70 mA h g^{-1} delivered from nitrogen-doped graphene aerogels and MnO_2 . This discharge capacity is superior to that of the previously reported MnO_2 /carbon based hybrid materials. This material also exhibited an excellent rate capability and cycling performance. Its superior electrochemical performance can be ascribed to the synergistic interaction between uniformly dispersed MnO_2 particles with high capacity and the conductive three-dimensional nitrogen-doped graphene network with a large surface area and interconnected porous structure.

Keywords: Manganese Dioxide; Nitrogen-Doped Graphene; Porous Material; Aerogel; Lithium Ion Battery.

Introduction

With the rapid development of portable electronic devices and electric vehicles, development of next generation rechargeable lithium ion batteries with high capacity and long cycling stability have attracted intensive interest.^{1,2} Graphite is a commonly used anode material due to its low cost, natural abundance and good cycling stability. However, it suffers from low theoretical capacity (372 mA h g^{-1}), retarding the development of more advanced lithium ion batteries.³

Nanostructured transition metal oxides with a high theoretical specific capacity and low cost are gaining wide spread attention.^{4,5,6,7,8,9} Manganese dioxide (MnO_2) is a particularly promising anode material owing to the high theoretical capacity (1230 mA h g^{-1}).^{10,11,12} However, the specific capacity, rate performance and cycling stability are still not satisfactory to date due to the low inherent conductivity and large volume changes during the charge/discharge processes.¹³ To overcome these obstacles, one common strategy is to prepare MnO_2 nanocomposites within a carbon matrix, which can act as both a conductive network increasing the electrical conductivity and a volume buffer to alleviate internal stress.^{14,15,16,17,18} The use of three-dimensional (3D) well-connected porous networks provide an additional benefit by shortening the ion diffusion length.^{19,20,21} A greatly improved battery performance is expected from MnO_2 /carbon composites with a porous structure.

Graphene aerogels have been widely investigated due to their large specific surface area, high electrical conductivity and 3D interconnected porous structure.^{22,23} For example, Wang et al. reported that MnO_2 /graphene aerogel composites prepared using an electrochemical method exhibited excellent capacitive characteristics including large specific capacitance (410 F g^{-1} at 2

mV s⁻¹), high rate capability and good cycling stability.²³ The use of nitrogen-doped graphene aerogel can further enhance electrochemical performance.^{24,25} The presence of nitrogen atoms at the carbon surface can alter the electronic performance and provide more active sites.^{26,27} For example, Tan et al. prepared a tin oxide/nitrogen doped graphene aerogel composites using a hydrothermal method, which displayed a remarkable lithium storage capacity of 1100 mA h g⁻¹ after 100 cycles at a current density of 200 mA g⁻¹.²⁸ Yin et al. reported that iron nitride (Fe_xN)/nitrogen doped graphene aerogel composites obtained from a hydrothermal method displayed an excellent catalytic activity in oxygen reduction reaction.²⁹ However, the work on MnO₂/nitrogen-doped graphene aerogel composites has not been reported for lithium ion batteries to date.

In this work, we reported the fabrication of MnO₂/nitrogen-doped graphene hybrid aerogel composites (MNGAs) via an easy redox reaction between KMnO₄ and carbon within nitrogen-doped graphene hydrogels (NGHs) for the first time. The as-prepared MNGAs as anode materials display a very high discharge capacity of 909 mA h g⁻¹ after 200 cycles at a current density of 400 mA g⁻¹. This result is superior to that previously reported 890 mA h g⁻¹ at 100 mA g⁻¹ for graphene-wrapped MnO₂-graphene nanoribbons,³⁰ 801 mA h g⁻¹ after 50 cycles at 200 mA g⁻¹ for MnO₂/carbon nanotube nanocomposite³¹ and 495 mA h g⁻¹ after 40 cycles at 100 mA g⁻¹ for graphene/MnO₂ nanotubes.³² Our samples also display excellent cycling performance and high rate capability. Such excellent performance can be ascribed to the synergistic effects of uniformly dispersed MnO₂ particles and the conductive three-dimensional porous nitrogen-doped graphene sheets.

Experimental section

Preparation of nitrogen-doped graphene hydrogels (NGHs)

Graphite oxide was prepared using natural graphite as the starting material via a modified Hummers' method, as described in the previous reports.^{33,34} The NGHs were prepared by a hydrothermal method. In a typical procedure, 4 mL of ammonia solution (28 wt%) was added to 18 mL of aqueous GO dispersion (5 mg mL^{-1}), then the mixture was sealed in a Teflon-lined stainless-steel autoclave. Black hydrogels were formed after the mixture was heated at 180°C for 12 h. The products, NGHs, were obtained after the black hydrogels were dialyzed to remove the impurities.

Preparation of NGAs and MNGAs

The MnO_2 /nitrogen-doped graphene hybrid aerogel composites (MNGAs) were fabricated through a facile redox reaction between KMnO_4 and carbon within NGHs. In a typical procedure, NGHs were immersed in a solution of 0.1 M KMnO_4 /0.1 M Na_2SO_4 . The above mixture was vigorously shaken in a shaker at room temperature to promote the diffusion of $\text{KMnO}_4/\text{Na}_2\text{SO}_4$ solution into NGHs and the spontaneous reaction between KMnO_4 and carbon in NGHs. After the reaction, the hybrid hydrogels were dialyzed with a great amount of deionized water for 48 h. The final products, MNGAs, were obtained by freeze-drying the hybrid hydrogels for 24 h under vacuum. An immersion time of 30, 60 and 120 min was applied to control MnO_2 loading. These samples were designated as MNGAs-x ($x = 30, 60$ and 120 min).

For comparison, nitrogen-doped graphene aerogels (NGAs) and MnO_2 were also prepared as

control samples. MnO_2 was obtained after MNGAs were calcinated at 400 °C for 6 h in air to remove the carbon component within the hybrid aerogel composites. NGAs were prepared by freeze-drying the NGHs for 24 h under vacuum prior to MnO_2 deposition.

Materials characterisation

A field emission scanning electron microscope (S-4800, Hitachi Ltd., Japan) was used to obtain the scanning electron microscopy (SEM) images, conducted at an accelerating voltage of 6 kV. Transmission electron microscopy (TEM) and high-angle annular dark-field scanning transmission electron microscope (HAADF-STEM) images were collected on a Tecnai G² 20 S-TWIN microscope (FEI, U.S.A.) with an accelerating voltage of 200 kV. X-ray diffraction (XRD) data were measured by a Philips X'Pert PRO X-ray diffraction instrument with a Cu K_α radiation generator. X-ray photoelectron spectroscopy (XPS) measurements were carried out on an ESCALab220i-XL electron spectrometer (VG Scientific Ltd., U.K.) using 300 W Al K_α radiation. Thermal gravimetric analysis (TGA) was operated on a Pyris Diamond thermogravimetric/differential thermal analyzer with a heating rate of 10 °C min⁻¹ in air. Raman spectra were recorded on a Renishaw inVia Raman spectrometer (Renishaw plc, U.K.) with 514 nm laser as excitation source. Nitrogen adsorption–desorption tests were carried out at 77 K on a Micromeritics TriStar II 3020 surface area and porosity analyzer (Micromeritics Instrument Corporation, U.S.A.). The as-prepared samples were degassed under vacuum at 120 °C for 12 h prior to measurement. The nitrogen adsorption–desorption isotherms were used to assess pore properties, including Brunauer–Emmett–Teller (BET) specific surface area, pore size distribution and pore volume.

Electrochemical measurements

The electrode was composed of active material (80 wt%), carbon black (10 wt%) and polyvinylidene fluoride (10 wt%) in *N*-methyl-2-pyrrolidinone. The resultant slurry was coated onto a copper foil substrate and dried at 80 °C for 12 h in a vacuum oven. The mass loading of electrode materials was typically in the range of 1.5–2 mg cm⁻². The electrode was assembled into LR 2032 type coin cells coupled with a lithium metal in a 1 M LiPF₆ electrolyte (1:1 v% ethylene carbonate and dimethyl carbonate). The galvanostatic charge/discharge tests were performed over a potential range of 0.005–3.0 V (vs. Li/Li⁺) on a LAND CT2001A battery test system (Wuhan Jinnuo Electronics Co. Ltd. China). Cyclic voltammetry was measured using a Solartron SI 1287 between 0.0 to 3.0 V (vs. Li/Li⁺) at a scan rate of 0.2 mV s⁻¹. Electrochemical impedance spectroscopy (EIS) measurements were carried out on a Gamry EIS 3000 system at open circuit potential over the frequency range of 0.01 Hz to 100 kHz.

Results and discussion

Fig. 1 Schematic procedures to prepare MNGAs.

NGHs were obtained by heating a mixture containing aqueous GO dispersion and ammonia

sealed in a Teflon-lined stainless-steel autoclave at 180 °C for 12 h, as illustrated in Fig. 1. Ammonia was the nitrogen source used to dope graphene sheets at high hydrothermal temperature.^{35,36} The formation of NGHs was driven by hydrogen bonding, π - π stacking and hydrophobicity interactions between nitrogen-doped graphene sheets.^{35,37} Subsequently NGHs were placed into the $\text{KMnO}_4/\text{Na}_2\text{SO}_4$ precursor solution and MnO_2 was formed via the spontaneous redox deposition: $4 \text{KMnO}_4 + 3 \text{C} + \text{H}_2\text{O} = 4 \text{MnO}_2 + \text{K}_2\text{CO}_3 + 2 \text{KHCO}_3$.^{38,39} The final products, MNGAs were obtained by freeze-drying of the hybrid hydrogels under vacuum for 24 h. The loading amount of MnO_2 was controlled by the immersion and reaction time. It was 16.1, 27.3 and 42.5 wt% in MNGAs-30, MNGAs-60 and MNGAs-120, respectively (estimated from the TGA curves in Fig. S1).

Fig. 2 SEM images of NGAs (a), MNGAs-30 (b), MNGAs-60 (c) and MNGAs-120 (d). Insets: SEM images at higher magnification.

NGAs exhibit a 3D network structure with interconnected pores (Fig. 2a). This porous

structure was maintained when the MnO_2 nanoparticles deposition time was 30 min (MNGA-30, Fig. 2b). When this increased to 60 and 120 min, the interconnected porous structure became less well defined. However, the porous structure can be observed at higher magnification (insets of Fig. 2c and 2d). Interestingly, no large MnO_2 particles or aggregates were observed at high magnification even for the sample MNGAs-120 with 42.5 wt% of MnO_2 .

The porous characteristics of NGAs and MNGAs were further studied by nitrogen adsorption–desorption measurements (Fig. 3). Both MNGAs and NGAs possess type IV adsorption–desorption isotherms with type H3 hysteresis loops (Fig. 3a), indicating that mesoporosity and slit-shaped pores exist in these hybrid aerogels. The BET specific surface area of these samples decreased with the increased MnO_2 loading. It was $820 \text{ m}^2 \text{ g}^{-1}$ for NGAs, which became 640 for MNGAs-30, 590 for MNGAs-60 and $490 \text{ m}^2 \text{ g}^{-1}$ for MNGAs-120. The pore volume decreased as well, from $1.61 \text{ cm}^3 \text{ g}^{-1}$ to 1.34, 1.25 and $1.12 \text{ cm}^3 \text{ g}^{-1}$, respectively. The decrease in the specific surface area and pore volume can be attributed to the increased loading amount of MnO_2 nanoparticles within the hybrid aerogel. According to Barret–Joyner–Halenda adsorption pore size distributions (Fig. 3b), most pore volume of NGAs, MNGAs-30, MNGAs-60, and MNGAs-120 lie in the 2–40 nm region and the main peak located at $\sim 2.3 \text{ nm}$. The formation of these nanosized pores can be ascribed to the 3D assembly of 2D graphene sheets during hydrothermal treatment, which has been observed previously.^{20,40}

Fig. 3 Nitrogen sorption isotherms (a) and Barret–Joyner–Halenda adsorption pore size distributions (b) of NGAs, MNGAs-30, MNGAs-60 and MNGAs-120 (solid symbols: adsorption; empty symbols: desorption). The isotherm of MNGAs-120 was offset by 150 units for clarity.

The successful deposition of MnO_2 particles onto nitrogen-doped graphene sheets can be revealed with TEM images (Fig. 4a–d). More MnO_2 nanoparticles can be observed on the nitrogen-doped graphene sheets with the increasing immersion and reaction time of NGHs in $\text{KMnO}_4/\text{Na}_2\text{SO}_4$ solution. Also no large aggregates can be found. The size of MnO_2 particles was $\sim 4\text{--}8\text{ nm}$ (Fig. 4e). The lattice spacing of MnO_2 nanoparticles was measured to be $\sim 2.4\text{ \AA}$ (Fig. 4f), which corresponded to that of (006) planes of birnessite MnO_2 .⁴¹ MNGAs-120 sample was chosen to investigate the dispersibility of MnO_2 nanoparticles within nitrogen-doped graphene matrices. A 3D porous network structure was observed (Fig. 4g and h), which is consistent with the SEM results. All the elements of C, N, O and Mn displayed a uniform distribution (Fig. 4i–l), further proving that MnO_2 nanoparticles were uniformly anchored onto the nitrogen-doped graphene sheets.

Fig. 4 TEM images of NGAs (a), MNGAs-30 (b), MNGAs-60 (c) and MNGAs-120 (d); TEM images of MNGAs-120 at high magnifications (e and f); HAADF-STEM image of MNGAs-120 at low (g) and high (h) magnifications; EDS mapping of C (i), N (j), O (k) and Mn (l).

The introduction of MnO_2 nanoparticles into nitrogen-doped graphene networks can also be detected using X-ray diffraction method. A broad peak centered at around 24° (ca. 0.37 nm of interlayer spacing) is observed for NGAs (Fig. 5a), indicative of the restacking of nitrogen-doped graphene sheets occurred during the freeze-drying process, which is in accordance with the

previous reports.³⁵ After the incorporation of MnO₂, the peak at around 24° becomes weaker and two new peaks appear at around 36.8° and 65.7°. These two peaks correspond to the (006) and (119) peaks of MnO₂ (JCPDF 18-0802), which further confirms the successful introduction of MnO₂ nanoparticles.

The chemical composition and more structural information were revealed by XPS and Raman spectroscopy. XPS reveals the presence of C, O and N in NGAs. An additional signal attributed to manganese (Mn 2p) appears in the MNGA samples (Fig. 5b), evidence of MnO₂ deposition onto the nitrogen-doped graphene sheets. The nitrogen content in NGAs, MNGAs-30, MNGAs-60, and MNGAs-120 is 8.1, 7.1, 6.6, and 6.1 atom %, respectively. The N 1s spectrum of MNGAs-120 (Fig. 5c) can be deconvoluted into three peaks, pyridinic (398.7 eV), pyrrolic (399.9 eV) and quaternary nitrogen (401.8 eV).⁴² In the high-resolution XPS spectrum of Mn 2p (Fig. 5d), MNGAs-120 display a Mn 2p_{3/2} peak at 642.2 eV and a Mn 2p_{1/2} peak at 653.9 eV with an energy separation of 11.7 eV. These two peaks of Mn 2p are consistent with the previously reported data.⁴³ NGAs and MNGAs display two strong characteristic peaks of carbonaceous materials in Raman spectra (Fig. 5e), *D*-band ($\approx 1350\text{ cm}^{-1}$) and *G*-band ($\approx 1590\text{ cm}^{-1}$), confirming the presence of graphene sheets.⁴⁴ Two obvious peaks (around 570 and 650 cm^{-1}) can be found in the low wavenumber region for all MNGAs samples. They correspond to the vibrations of oxygen ions in the manganate lattice, further confirming the incorporation of MnO₂ nanoparticles.^{45,46}

Fig. 5 XRD patterns (a) and XPS survey scan spectra (b) of NGAs and MNGAs; N 1s (c) and Mn 2p XPS spectra (d) of MNGAs-120; (e) Raman spectra of NGAs and MNGAs.

The electrochemical process of the lithiation and delithiation of NGAs and MNGAs was investigated using cyclic voltammetry at a scan rate of 0.2 mV s^{-1} . An irreversible reduction peak appears at around 0.5 V in the first cycle for all these samples (Fig. 6), and this is attributed to the formation of a solid electrolyte interphase (SEI) layer at the electrode surface.^{47,48} This peak disappears in the following cycles. Compared to NGAs, a sharp cathodic peak at around 0.3 V is observed for all the MNGAs samples. This is attributed to the reduction reaction of MnO_2 (MnO_2

+ 4 Li⁺ + 4 e⁻ → 2 Li₂O + Mn). These MNGAs electrodes display two anodic peaks at 1.2 and 2.0 V. These two anodic peaks might be ascribed to two oxidation processes from MnO₂, Mn⁰ to Mn²⁺ and Mn²⁺ to Mn⁴⁺.⁴⁹

Fig. 6 (a) Cyclic voltammograms (CV) of the first three discharge/charge cycles for NGAs (a), MNGAs-30 (b), MNGAs-60 (c) and MNGAs-120 (d) at a scan rate of 0.2 mV s⁻¹ between 0.0–3.0 V.

The first three discharge/charge cycles for NGAs and MNGAs at 100 mA g⁻¹ are illustrated in Fig. 7a–d. The initial discharge capacity of NGAs, MNGAs-30, MNGAs-60 and MNGAs-120 is 1090, 924, 1026 and 1172 mA h g⁻¹. Their initial charge capacity is 608, 648, 786 and 937 mA h g⁻¹, corresponding to a Coulombic efficiency of 56 %, 70 %, 77 % and 80%. At the 3rd cycle, the discharge capacity of NGAs, MNGAs-30, MNGAs-60 and MNGAs-120 is 567, 691, 775 and 941 mA h g⁻¹, displaying a Coulombic efficiency of 92 %, 91 %, 95 % and 96 %, respectively. The

large capacity loss can be ascribed to the formation of SEI layer, which is in agreement with CV results. This clearly demonstrates that the discharge capacity and Coulombic efficiency are greatly improved after the incorporation of MnO₂ nanoparticles into NGA matrices. The enhanced performance can be explained by the synergistic interaction between MnO₂ nanoparticles and the conductive nitrogen-doped graphene network with an interconnected porous structure. The contribution from uniformly distributed MnO₂ nanoparticles include additional high capacity and a spacer to prevent the severe restacking of graphene nanosheets. The 3D conductive nitrogen-doped graphene sheets can improve the poor conductivity of MnO₂. The presence of nitrogen atoms is also beneficial to the storage capacity of lithium ions.²⁷

The rate capability of MNGAs and NGAs was studied at different current density of 100, 200, 400, 600, 800, 1000 and 1500 mA g⁻¹ (Fig. 7e). For MnO₂ sample, it delivers an initial discharge capacity of 959 mA h g⁻¹ at a current density of 100 mA g⁻¹ and only remains 24 mA h g⁻¹ at a current density of 1500 mA g⁻¹ after 70 cycles, a 2.5 % capacity retention. While for MNGAs samples, they show excellent rate capability compared to that observed for pure MnO₂ or NGAs. NGAs, MNGAs-30, MNGAs-60 and MNGAs-120 electrodes show a discharge capacity of 461, 649, 716 and 1003 mA h g⁻¹ at a current density of 100 mA g⁻¹, respectively. The capacity turns to be 276, 435, 571 and 846 mA h g⁻¹ at a current density of 400 mA g⁻¹, respectively. MNGAs-120 electrodes exhibit the highest discharge specific capacity and rate capability. The discharge/charge curves of NGAs, MNGAs-30, MNGAs-60, and MNGAs-120 electrodes at different current densities were also given in Fig. S2. It can still deliver a discharge capacity of 636 mA h g⁻¹ at a current density of 1500 mA g⁻¹, which is 3.9 times higher than that (162 mA h g⁻¹) of NGAs. As

the current density returns back to 100 mA g^{-1} , MNGAs-120 electrodes deliver a discharge specific capacity of 1095 mA h g^{-1} , slightly higher than the initial reversible capacity.

Fig. 7 The first three discharge/charge cycles of NGAs (a), MNGAs-30 (b), MNGAs-60 (c) and MNGAs-120 (d) at the current density of 100 mA g^{-1} ; (e) rate capacity curves of NGAs, MnO_2 and MNGAs between 0.005 V and 3.0 V at various current densities; (f) capacity vs. cycle number curves of NGAs, MnO_2 and MNGAs at the discharge current of 400 mA g^{-1} . (Note: The first cycle is not included.)

The cycling performance of NGAs and MNGAs was tested at a current density of 400 mA g^{-1}

(Fig. 7f). The discharge capacity of MNGAs increases with an increase of MnO_2 loading. Their Coulombic efficiency approaches 100 % after a few cycles (Fig. S3). For MnO_2 sample, the reversible capacity was only 70 mA h g^{-1} after 200 cycles, a 48 % capacity retention. This sharp capacity decay can be ascribed to the particle pulverization during the repeated lithiation and delithiation processes. MNGAs-30, MNGAs-60 and MNGAs-120 electrodes show a discharge capacity of 467, 627 and 909 mA h g^{-1} after 200 cycles, in sharp contrast to MnO_2 (70 mA h g^{-1}) and NGA (280 mA h g^{-1}). This enhanced electrochemical performance suggests that nitrogen-doped graphene sheets in a porous structure can effectively alleviate the volume changes of MnO_2 nanoparticles during the lithiation and delithiation processes. In addition, the presence of nitrogen can enhance the battery performance by introducing more defects.²⁶ These defects are beneficial to the adsorption of lithium ions and the penetration of lithium ions into the interior of the electrode, thus increasing the storage capability of lithium.²⁷ It is also noticed that the discharge capacity of MNGAs electrodes increased slightly with the cycling number. It can be explained that the electrolyte can access this composite in depth after the lithiation and delithiation processes and offer higher electrochemical activity.³⁰

The EIS measurements were used to study the charge transport kinetics of MnO_2 and hybrid aerogel composites. As shown in Fig. 8a, the Nyquist plots of MnO_2 and MNGAs consist of a semicircle (high frequency region) attributed to the charge transfer resistance at the electrode/electrolyte interface and a straight line (low frequency region) related to lithium ions diffusion in the bulk materials. All MNGAs samples possess a much smaller semicircle than MnO_2 , indicating that 3D porous structure of nitrogen-doped graphene network can reduce the electron

transfer resistance and enhance the ion and electron kinetics. It can be used to explain the improved electrochemical performance driven from those composites. It was also noticed that NGAs possess a much smaller semicircle than MNGAs-120. However, MNGAs-120 electrodes display much higher discharge capacity. The greatly improved capacity can be ascribed to the introduction and contribution of MnO_2 with high theoretical capacity.

Fig. 8b shows the scheme of the possible structure for MNGAs electrodes. The significantly improved lithium storage capability, high-rate performance and cycling stability of MNGAs can be ascribed to the synergistic interaction between uniformly dispersed MnO_2 particles and the 3D conductive nitrogen-doped graphene network. (1) The porous network of nitrogen-doped graphene sheets provides a mechanical support to alleviate the volume changes associated with MnO_2 nanoparticles during the lithiation and delithiation processes. (2) The 3D connected graphene-based matrix can work as a conductive layer to reduce the charge transfer resistance, thus enhancing the ion and electron kinetics. (3) The open porous structure of MNGAs can facilitate easy access of electrolyte and also a shortened ion diffusion length. (4) Nitrogen-doping leads to more defects, which can provide more adsorption sites for lithium ions and also promote the penetration of lithium into the interior of the electrode.

Fig. 8 (a) The electrochemical impedance spectra of NGA and MNGAs electrodes; and (b) schematic illustration of structure for MNGAs electrodes.

Conclusions

3D porous MNGAs have been prepared via a facile process involving KMnO_4 and carbon from NGHs. MnO_2 nanoparticles were incorporated into a 3D porous network of NGHs and were uniformly dispersed on nitrogen-doped graphene sheets. These samples possess a very high specific capacity, excellent rate performance and cycling stability compared to NGAs and MnO_2 samples. Such superior electrochemical properties can be ascribed to the unique conductive 3D porous structure, which can not only alleviate the volume expansion of MnO_2 nanoparticles but also enhance the charge transfer. The shortened ion diffusion path and enhanced electron transfer from nanosized MnO_2 particles as well as nitrogen-doping contribute to the enhanced performance. Other inorganic nanoparticles might be incorporated into nitrogen-doped graphene aerogel through this facile method, such as MoO_2 , Co_3O_4 and SnO_2 . These hybrid aerogel composites may hold promise in the fields of supercapacitors, batteries and catalysis.

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Electronic supplementary information (ESI) available: TGA curves of MNGAs-30, MNGAs-60 and MNGAs-120 under air atmosphere; the discharge/charge curves of NGAs, MNGAs-30, MNGAs-60 and MNGAs-120 electrodes at different current densities (100, 200, 400, 600, 800, 1000 and 1500 mA g⁻¹); Coulombic efficiency of NGAs, MNGAs-30, MNGAs-60 and MNGAs-120 at a current density of 400 mA g⁻¹.

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Table of Contents/Abstract Graphic

MnO_2 /nitrogen-doped graphene aerogels prepared *via* a redox process between KMnO_4 and carbon demonstrate excellent electrochemical properties in Li-ion batteries.