Synthesis of Nitrogen-Doped Mesoporous Structures from Metal–Organic Frameworks and Their Utilization Enabling High Performances in Hybrid Sodium-Ion Energy Storages

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Sodium-ion energy storage is of the most attractive candidate for commercialization adoption due to the safety and cost demands of large-scale energy storage systems, but its low energy density, slow charging capability, and poor cycle stability are yet to be overcome. Here, a strategy is reported to realize high-performance sodium-ion energy storage using battery-type anode and capacitor-type cathode materials. First, nitrogen-doped mesoporous titanium dioxide (NMTiO2) structures are synthesized via the controlled pyrolysis of metal–organic frameworks. They exhibit interconnected open mesopores allowing fast ion transport and robust cycle stability with nearly 100% coulombic efficiency, along with rich redox-reactive sites allowing high capacity even at a high rate of \( \approx 90 \text{ C} \). Moreover, assembling the NMTiO2 anode with the nitrogen-doped graphene (NG) cathode in an asymmetric full cell shows a high energy density exceeding its counterpart symmetric cell by more than threefold as well as robust cycle stability over 10 000 cycles. Additionally, it gives a high-power density close to 26 000 W kg\(^{-1}\) outperforming that of a conventional sodium-ion battery by several hundred fold, so that full cells can be charged within a few tens of seconds by the flexible photovoltaic charging and universal serial bus charging modules.

Beyond the increasing demand for electric vehicles (EVs) and portable devices,[1] a rechargeable electrochemical energy storage system (ESS) is an essential component of many applications. Nowadays, the dominating ESS remains on a lithium-ion battery (LIB),[2] but the more challenging requirement for a future ESS continues to drive development of next-generation ESS. In hybrid energy storages, charges are asymmetrically stored by ion adsorption and pseudocapacitive interaction in cathode and anode materials, respectively, so that their charge and discharge processes can be controlled using different potential windows to increase energy density.[7] Moreover, low-cost hybrid energy storages can be developed using an earth-abundant electrolyte including sodium (Na) ions.[8–11] However, many electrode materials suffer from several obstacles such as safety and poor capacity in a sodium-ion electrolyte. Titanium dioxide (TiO2) is considered as a promising anode material for a hybrid energy storage as it is capable of being operated at a low potential that is advantageous for safety. The problem is that it gives poor electronic conductivity and ionic diffusivity, thus resulting in fast capacity fading and short cycle life.[12–19] Consequently, a new strategy that can overcome the current limitations of such an electrode material is expected to represent a great breakthrough in the development of high-performance sodium-ion electrochemical energy storages.

Herein, we realize hybrid sodium-based electrochemical energy storages on a new paradigm strategy, where both a nitrogen-doped mesoporous TiO2 (NMTiO2) structure synthesized through the controlled pyrolysis of a metal–organic framework (MOF) and also a nitrogen-doped graphene (NG) were utilized as anode and cathode materials, respectively. The nitrogen-doped mesoporous NMTiO2 structures are shown to give excellent energy density, high power density allowing ultrafast charging, and robust cycle stability over 10 000 cycles. An MOF has the secondary building units (SBUs) that could play potentially as active sites for electrochemical redox reactions. Also, its tunable porosity and functionality could offer fast ion transport pathways by enabling the facile accessibility of ion transport...
carriers to active sites. Moreover, the unique structures and properties of the NMTiO₂ can be summarized as follows: 1) it contains open mesopores (∼4 nm) enabling an easy penetration of electrochemical Na-ion carriers between the electrolyte and active sites; 2) ultrafine nanocrystals with nitrogen-doped TiO₂ units can be encapsulated inside its interior parts, which establish excellent stability at the fast charging rate such as ∼90 C (30 000 mA g⁻¹) with negligible capacity reduction over a long cycle life; and 3) the heterogeneous N atoms in its matrix lead to enhanced electrochemical ion sorption/desorption during repeated charge–discharge cycles. Also, a NG, having many heterogeneous N atoms in the carbon matrix and facilitating the accessibility of anions, was employed as the cathode material to achieve high capacity. Furthermore, the NMTiO₂//NG full cell is configured into a hybrid asymmetric configuration to demonstrate high energy density and robust cycle stability. Additionally, the flexible photovoltaic charging and USB charging modules are realized to demonstrate the ultrafast charging capability of NMTiO₂//NG full-cell devices.

A microwave-assisted solvothermal method was used to prepare the NH₃·MIL-125 (Ti) represented by the chemical formula of Ti₉O₄(OH)₆(CH₃C₆H₄O₂)NH₃₆ with a short reaction duration. During the synthesis, the functional groups of the NH₃ions and Ti⁺⁴ ions in ligands (CH₃C₆H₄O₂)₃ and SBUs (Ti₂O₂(OH)₄) serve as the heterogeneous dopants and metal resources, respectively. In addition, the nanocages in MOFs play an important role in introducing mesopores.[20,21] The simple synthetic procedures of the anode and cathode materials for the full-cell configuration and their energy storage mechanisms are shown in Figure 1 as schematics. The 3D mesoporous architecture having uniform sized nanoparticles (NPs) of nitrogen-doped TiO₂ units was successfully synthesized through the simple pyrolysis of MOFs in air condition, and Figure 1a shows that it maintains the original morphology of an MOF. The carbon species in the functional ligands were also removed during the thermal oxidation procedure, while mesopores were introduced in the remaining spaces. The amine functionalized–titanium MOFs were used as the template to obtain nitrogen-doped mesoporous TiO₂ NPs. It is found that the diffusion of sodium ions in a salt-containing electrolyte is facilitated by the introduced mesopores in the NMTiO₂. Furthermore, the nitrogen-doped graphene was synthesized as a cathode material by plasma treatment with nitrogen gas (Figure 1b). The NG has a high active surface area from its 2D morphology. Also, the radius of 0.74 Å for a N atom is similar to that of 0.77 Å for a C atom so that N atoms are easily doped into the carbon matrix of graphene. Moreover, the electronegativity of 3.04 for N is higher than that of 2.5 for C so that heterogeneous nitrogen dopants modify the electronic distribution of the carbon matrix of graphene to improve electrical conductivity as well as provide abundant active sites for redox reactions.[22,23] The illustration of the NMTiO₂//NG full cell and the corresponding energy storage mechanisms between the electrolyte and electrode atoms is presented in the schematics (Figure 1c,d). The titanium-based MOFs were synthesized through the microwave-assisted solvothermal technique having great advantages such as the high heating rate and short reaction time. In brief of methods, titanium isoproxide (0.6 mmol) and 2-aminoterephthalic acid (1.2 mmol) were dissolved in a mixed solvent of N,N-dimethylformamide (DMF) and methanol (MeOH) (20 mL; DMF:MeOH = 1:1 in volume), and then put into a 35 mL glass tube, which is capped by a rubber septum and placed in a microwave synthesizer. Next, the mixture was heated to 150 °C, held for 1 h, and then cooled to room temperature. The yellow product was washed with DMF and methanol several times. Also, the powder was dried and evacuated in vacuum oven at 60 °C. After that, the powder of the NH₃·MIL-125 (Ti) was placed in an alumina boat under the steady air-flow condition. Moreover, the sample was annealed to 350 °C, kept for 2 h, and then cooled to room temperature. The product is a light-yellow-colored powder, which is ascribed to nitrogen dopants playing to result in the decreased bandgap from 3.24 to 2.78 eV.[24] The bandgap and coloring of the nitrogen-doped TiO₂ were investigated by UV–vis absorption spectra and real photo images, and Figure S1 (Supporting Information) shows the shift of observation spectra owing to the reduced bandgap by ∼0.54 eV and the light yellow color on nitrogen doping. It is notable that the nitrogen-doped TiO₂ NPs are formed, and the mesopores between particles are introduced during the thermal oxidation process. Mesopores in the negative electrode (Figure 1c) allow a facile access of Na⁺ ions to nitrogen-doped TiO₂ units, while heterogeneous N atoms in the carbon matrix of the NG facilitate the accessibility of ClO₆⁻ ions in the positive electrode (Figure 1d).

Figure 2a shows the scanning electron microscope (SEM) image of the NH₃·MIL-125 (Ti). The rectangular parallelepiped shapes with round edges are clearly observed. The mesoporous NMTiO₂, which was synthesized at a low temperature through the pyrolysis of the NH₃·MIL-125 (Ti), has a uniform shape and size, and its morphology is quite similar to that for the NH₃·MIL-125 (Ti) (Figure S2, Supporting Information). The transmission electron microscope (TEM) and scanning TEM (STEM) images (Figure 2b; Figure S3, Supporting Information) further reveal a highly porous feature arising from the voids between its nanocrystals, implying that nanocrystals are homogeneously formed during the annealing procedure without leading to the structural collapse of the framework. The size of the NMTiO₂ is also determined to be at an average size of 500 nm, and it has the average thickness of 140 nm. Figure 2c also shows a high-resolution TEM (HRTEM) image elucidating the ∼7 nm size of a titanium nanocrystal with the lattice spacing of 0.346 nm corresponding to the (101) plane of the anatase phase. Additionally, the selected area electron diffraction (SAED) pattern of an individual framework (inset of Figure 2c) reveals the circular patterns showing a polycrystalline anatase.[25] Such a highly crystalline framework ensures good mechanical robustness during electrode cycling. The constituents of the NMTiO₂ are mainly Ti and O species, and also include nitrogen and carbon atoms, as confirmed from the STEM–energy dispersive spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS) analyses (Figures S4 and S5, Supporting Information). The STEM–EDS mapping images further show that each constituent is uniformly distributed throughout the sample. The XPS spectra of the NMTiO₂ sample show the distinct peaks corresponding to C 1s, O 1s, Ti 2p, and N 1s at ~283, 529, 463, and 398 eV, respectively. Furthermore, the STEM–EDS analysis of the NG (Figure S6, Supporting Information) presents the uniformly distributed C, O, and N species as the constituent elements of...
Figure 1. The schematics of all synthetic processes, mechanisms, and cell configurations. a) The schematics for the synthesis of a nitrogen-rich mesoporous metal oxide anode material (NMTiO$_2$) from the nitrogen-functionalized metal–organic framework (NH$_2$-MIL-125 (Ti)) via a facile pyrolysis process. The titanium ions were thermally oxidized with oxygen ions in the air so that it could maintain its original morphology. b) The schematics for synthesis of a nitrogen-doped graphene (NG) cathode material via a nitrogen plasma treatment. The synthesized c) NMTiO$_2$ anode and d) NG cathode materials assembled into a hybrid sodium-ion energy storage full cell and the corresponding energy storage mechanisms for charge carriers in anode and cathode structures.
the NG, while the XPS analysis (Figure S7, Supporting Information) of the NG for C 1s (≈284 eV), O 1s (≈531 eV), and N 1s (≈399 eV) demonstrates the sharp peak of N 1s indicating the existence of rich nitrogen atoms in the graphene sheets, so that they provide rich active sites for the electrochemical reactions with the ions in the electrolyte. In addition, the high-resolution STEM image (Figure 2d) shows the open mesopores created at the TiO₂ nanocrystal interfaces. Moreover, the high-resolution STEM pore image in Figure 2e demonstrates that the mesopores with an average size of ≈4 nm were created. This feature is especially advantageous to give high rate capability and long-term cycling stability due to the facilitated diffusion of electrolyte ions through the open mesopores. Furthermore, the crystallographic information for NMTiO₂ and bare NH₂-MIL-125 (Ti) structures was collected via the X-ray diffraction (XRD). The high-crystalline NH₂-MIL-125 (Ti) was also confirmed from the sharp diffraction peaks attributed to the micropores in Figure S8a (Supporting Information).[26] The diffraction peaks (Figure 2f) at 25.3°, 37.8°, 48.2°, and 54.6°, corresponding to (101), (004), (200), and (211) planes, are well matched with those for the anatase TiO₂ (JCPDS card No. 21–1272). However, for the lower-temperature-annealed sample, the diffraction peaks of the rutile TiO₂ (JCPDS card No. 21–1276) were not observed and the peaks are on more
broad shapes and lower intensities, implying that the NMTiO2 could be synthesized to have a smaller particle size and a single anatase phase in the lower temperature. Also, a nitrogen sorption analysis at 77 K (Figure 2g) clarifies that the NMTiO2 possesses rich mesopores centered at the pore diameter of ~4 nm, which is in a suitable size to enable the large uptake of electrolyte ions for fast ionic transport and also agree well with the pore sizes by the high-resolution STEM images. Moreover, the isotherm analysis (Figure S8b, Supporting Information) shows that NH3-MIL-125 (Ti) has a high surface area (1146.3 m² g⁻¹). The nitrogen dopants in the NMTiO2 were further investigated by XPS analyses and the Fourier transform infrared spectroscopy (FT-IR). The N 1s peak at 399.2 eV (Figure 2h) is attributed to N—Ti—N bonds formed by the substitutional doping of the O atoms in O—Ti—O bonds by N atoms. Furthermore, the Ti—N—O bonding formed the interstitial nitrogen dopants in the anatase TiO2 lattice is also confirmed by the peak at ~401 eV. Figure 2i and Figure S9 (Supporting Information) also show the band at ~1080, 1250, 1390, and 1475 cm⁻¹ attributed to the vibrations of Ti—N bonds as well as the band of 1630 cm⁻¹ corresponding to the N—H bending vibration. The band of vibration from the surface-absorbed NO3⁻ was also confirmed at around 1390 cm⁻¹. In addition, the broad band at ~3400 cm⁻¹ is shown to match with the spectra of the surface hydroxyl groups and absorbed water molecules. The band at ~2340 cm⁻¹ is attributed to the C=N=O asymmetric stretch. From these results, the appearance of the vibration bands related to the nitrogen bindings such as Ti—N, Ti—N=O, and N—Ti—N bonds supports that the nitrogen species were successfully incorporated in the lattice of TiO2 NPs.

To investigate the morphological influence on the cell performance, we synthesized the products at different processing temperatures and reaction times such as from 350 to 500 °C and from 30 min to 2 h, respectively. Figure S10 (Supporting Information) shows the thermal oxidation behavior of NH2-MIL-125 (Ti) under the air flow conditions. In the first range below ~335 °C that is the crystallization temperature of titanium ions, we find that small amounts of surface-absorbed water molecules and impurities were removed. After then, the crystallization of titanium ions and the combustion of carbon species were observed to be occurring up to ~550 °C. These results imply that the thermal oxidation of titanium ions could be proceeded above 335 °C. The electrochemical performances for NMTiO2 and NG were also evaluated in coin-type half-cells connected mesopores in the TiO2 anode, thereby allowing high energy storage capacity and fast sodiation/desodiation. Figure 3g shows further that the NMTiO2 electrode gives high capacity even at an ultrafast charging rate (~90 C). The galvanostatic intermittent titration technique (GITT) measurements were also analyzed to determine the diffusion kinetics of Na⁺.

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mesoporous TiO$_2$ synthesized at the low annealing temperature can give the facilitated Na-ion diffusion between the surface and the electrolyte.\cite{36,37}

Figure S13 (Supporting Information) also clarifies the electrochemical performance of the NG cathode in a half-cell configuration investigated with the Na foil as a counter electrode in
the working potential window of 3–4.5 V. The CV curve shows a typical capacitive behavior and the gravimetric measurements demonstrate the maximum capacity of ~78 mAh g⁻¹.

We also realized the NMTiO₂//NG sodium-ion full-cell device (Figure 4a). The charge carriers such as Na⁺ and ClO₄⁻ ions in the electrolyte can be easily diffused through the introduced mesopores in the NMTiO₂ and electrochemically interacted with both electrodes by heterogeneously doped nitrogen species. The NMTiO₂ with rich nitrogen and mesopore cages was used as the anode and coupled with the cathode made of NG nanosheets. The weight ratio of electrode materials for anode and cathode was optimized as m_anode:m_cathode = 1:3.5 by matching charge balance. Figure 4b,d displays the CV curves for anode and cathode half-cells as well as the assembled full cell at the scan rate of 1 mV s⁻¹. The curves for anode and cathode with distinct redox peaks could be determined. The CV curves for the full cells demonstrate the charge storage mechanism attributed to the combination of Faradaic and non-Faradaic reactions. The energy storage mechanisms have also been explored by the galvanostatic charging/discharging profiles of anode and cathode electrodes (Figure 4c). The NMTiO₂ anode shows the Faradaic reaction curve for Na⁺ insertion/desorption, while the NG cathode gives the capacitive reaction curve. While symmetric NG//NG full-cell devices using organic electrolytes have the limited operation potential of 2.5 V due to the electrolyte decomposition,[38] the operating potential of 1–3.8 V for the assembled NMTiO₂//NG full cell is determined to allow higher energy density and stable operation. Figure 4e shows the galvanostatic charge–discharge profiles of full cells at different current densities. The linear curves of voltage profiles indicate typical capacitive behaviors during charging and discharging reactions. The calculated performance (Figure 4f) allows higher energy density and stable operation. Figure 4g also demonstrates the maximum capacity of 10 C at the power density of 91.1 W kg⁻¹. Also, it gives the high power density up to 25 920 W kg⁻¹ at a condition of ~20 C (7 A g⁻¹) outperforming that of a conventional sodium-ion battery by more than 400 folds. The results clarify that the NMTiO₂//NG full cells outperform the other full-cell devices of same materials such as TiO₂//NaLi₂Ni₄S₂Mn₄O₁₇,[39] Na₂Ti₂O₇/Na₂V₃(PO₄)₂F₇,[40] Na₂Ti₃(PO₄)₄/Na₂V₃(PO₄)₂F₇[41] Li₂TiO₂[Na₂V₃(PO₄)₂F₇,[42] Na₂Ti₂O₇/Na₂[V₂(PO₄)₃]O₇[43] and Na₂Ti₂O₇/GO (graphene oxide (GO) film)[44] in the Ragone plots, demonstrating the exceptional energy and power density performances. In addition, the highest energy density of the asymmetric NMTiO₂//NG full cell exceeds that of a typical sodium-ion battery by more than threefold, the high power density of 25 920 W kg⁻¹ exceeding that of a general sodium-ion battery by several hundred fold, and robust cycle stability over 10 000 charge–discharge cycles with excellent capacity retention. Moreover, the NMTiO₂//NG full-cell devices were demonstrated to be chargeable within a few tens of seconds by the USB LED charger and flexible photovoltaic charging module. These results support that the hybrid sodium-ion energy storage full cells assembled with nitrogen-doped mesoporous anode and nitrogen-doped graphene cathode electrodes provide rich active sites and rapid transport pathways for electrons and ions during repeated charging–discharging cycles, so that they show remarkably high energy density, ultrafast charging capability on excellent power density, and robust cycle stability over a long cycle life. Consequently, we expect that our findings provide a new solution to realize high-performance electrode materials from metal–organic frameworks, thus, adaptable to develop a diverse range of metal oxides usable for high-performance energy storage devices.

### Experimental Section

**Synthesis of NH₂-MIL-125(Ti):** Titanium isopropoxide (0.66 mmol) and 2-aminoentetraphenolic acid (1.2 mmol, H₂BDC-NH₂) were dissolved in a mixed solvent of N,N-dimethylformamide and methanol (20 mL, DMF:MeOH = 1:1 in volume), and then put into a 35 mL glass tube, which was capped by a rubber septum and placed in a microwave oven (Discover S-class, CEM). The mixture was heated to 150 °C, held for 1 h, and then cooled to room temperature. The yellow powder product was separated by centrifugation. After washing with DMF several times, the product was stored in methanol. The product was dried and evacuated in vacuum oven at 60 °C for 1 day.

**Pyrolytic Conversion of NH₂-MIL-125 (Ti) to NRTiO₂:** The powder products of the NH₂-MIL-125 (Ti) were placed in an alumina boat, placed within box furnace with a fixed air flow. Under the steady air flow, the samples could be decomposed by thermal oxidation reaction. The sample was annealed to 350 °C, kept for 2 h, and then cooled to room temperature. The product appeared as a light-yellow powder. In order to obtain a highly porous structure, this annealing procedure was conducted at a relatively low temperature and long reaction time considering the crystallization temperature.

**Synthesis of NG:** The NG was prepared via the nitrogen plasma treatment of a reduced graphene oxide (RGO), where GO nanosheets were synthesized by Hummers’ method. The graphite flake (5 g) and...
Figure 4. The electrochemical performances of full cells. a) The full-cell configuration illustrates that Na\(^+\) and ClO\(^-\) ions in the electrolyte have electrochemical interactions with both the anode structure having mesoporous channels and also the cathode structure having heterogeneously doped nitrogen species. b) The CV profiles of half-cells prepared from NMTiO\(_2\) anode and NG cathode materials. c) The charge–discharge profiles of NMTiO\(_2\) and NG in half-cell configurations. d) The CV profiles of the NMTiO\(_2\)/NG full cells on the various scan rates (mV s\(^{-1}\)). e) The charge-discharge profiles on different current densities (A g\(^{-1}\)). f) The Ragone plot (refs: TiO\(_2\)/Na\(_{1/3}\)(Ni\(_{1/3}\)Mn\(_{2/3}\))O\(_2\),\(^{[39]}\) Na\(_4\)Ti\(_6\)O\(_{13}\)/Na\(_3\)V\(_2\)(PO\(_4\))\(_2\),\(^{[40]}\) Na\(_2\)Ti\(_3\)O\(_7\)/Na\(_3\)V\(_2\)(PO\(_3\))\(_3\),\(^{[41]}\) Li\(_4\)Ti\(_5\)O\(_{12}\)/Na\(_3\)V\(_2\)(PO\(_3\))\(_3\),\(^{[42]}\) Na\(_2\)Ti\(_3\)O\(_7\)/Na\(_3\)V\(_2\)(PO\(_3\))\(_3\),\(^{[43]}\) and Na\(_2\)Ti\(_3\)O\(_7\)/GF\(^{[44]}\)). g) The capacity retention (inset: demonstrated photovoltaic charging and LED modules).
sodium nitrate (2.5 g, NaNO₃) were dissolved in concentrated sulfuric acid (120 mL, H₂SO₄), and the mixture was stirred during 20 min. Then, potassium permanganate (15 g, KMnO₄) was slowly added into the mixture in the ice bath below 20 °C, where it was maintained for 15 min, and then it was stirred for 4 h under 40 °C. After then, deionized water (100 mL) was slowly added into the mixture, where it was maintained for 1 h. The mixture was cooled to room temperature and hydrogen peroxide (2 mL, H₂O₂) was added into the mixture. The mixture was washed via vacuum filtration with hydrochloric acid (HCl), acetonitrile, and DI water, respectively. The product was dried via freeze drying for further use. Finally, the GO solution (1 mg mL⁻¹) was chemically reduced with hydrazine (1 mL mL⁻¹) as a reduction agent in oil bath at 80 °C. Then, the product was filtered and dried following the same method as for a GO product. The RGO solution was drop-casted onto a glass, and put into plasma-enhanced chemical vapor deposition (PECVD). Then, hydrogen and nitrogen gas plasmas were sequentially applied for 3 and 10 min, respectively.

**Characterization:** The morphology and structures of the samples were analyzed by the field emission SEM (Hitachi, SU-3000) and the high-resolution STEM–EDS (JEM, ARM2000F, Cs-corrected STEM). The TEM specimens were prepared by dropping the dispersed samples in volatile solvents on the TEM grid (Ted Pella Inc.) The X-ray diffraction data were collected using a SmartLab 9–2θ diffractometer in reflectance Bragg–Brentano geometry. The diffractometer used a Johansson-type monochromator filtering Cu Kα radiation at 120 W (40 kV, 30 mA) to minimize line broadening and was equipped with a high-speed 1D detector (D/teX Ultra). The 2θ range was 3°–90°. The surface chemical states were investigated by the XPS (Thermo VG Scientific Sigma Probe) analysis. Moreover, the porosity was analyzed through N₂ adsorption/desorption isotherm measurements at 77 K using the Brunauer–Emmett–Teller (Quantachrome Quadrasorb-evo). The chemical bonding information for the functional groups present in samples was also elucidated by using an FTIR spectroscopy (FT/IR-6100, JASCO) analysis. The NMTiO₂ and reference samples were ground with KBr using a mortar and a pestle in the ratio of 1:100 in weight, and then the mixture was pressurized through the hand-operated pressurization to the thin pellet having the width of 4 mm. The spectra were obtained at 2 cm⁻¹ with 50 scans per spectrum in the range of 500–4000 cm⁻¹. The thermal behavior of NH₂-MIL-125 (Ti) during the thermal oxidation procedure was investigated by thermogravimetric analysis (NETZCH TG 209 F1 Libra) in a range of 20–700 °C under 5 °C min⁻¹ heating rate and air flow conditions. To investigate the changes on nitrogen doping effects, the diffused absorption spectra were obtained by a VARIAN Cary® 300 UV–vis spectrophotometer using powder samples as prepared.

**Electrochemical Characterization:** The electrochemical properties of the NMTiO₂ and NG were characterized by using the 2032-type coin cells in which Celgard 2400 and Na foil were used as separators and counter/reference electrodes, respectively. On the sample preparation, the active material, super P, and polyvinylidene fluoride (PVDF) (80:10:10 in weight) were dispersed in N-methyl-2-pyrrolidone (NMP) to form a slurry. Then, the slurry was cast onto the Cu or Al foil using the doctor blade technique. The cast electrodes were dried in a vacuum oven at 80 °C overnight. The standard organic electrolyte was used in which the 1 m NaClO₄ was dissolved in ethylene carbonate (EC) and diethyl carbonate (DEC) (EC:DEC = 1:1 in volume). The entire cell preparation steps were conducted in an argon-filled glove box with the moisture content and oxygen levels less than 1 ppm. All of the electrochemical performance measurements were done at room temperature using a potentiostat/galvanostat/EIS system (VSP, Bio-Logic). Moreover, electrochemical analyses of the half-cells were measured in an operating potential range of 1–3 V (anode) and 3–4.5 V (cathode) versus Na/Na⁺, respectively. The impedance analysis was conducted in a frequency range from 0.01 Hz to 1000 kHz with the amplitude of 5 mV. The GITT measurements were carried out at –0.1 C in a period of 1 min. Before the measurements, the pre-sodiation procedure was conducted by attaching the NMTiO₂ electrode with the Na foil during 1 h. The mass loading was measured by the ultra-microbalance (XP2U, Mettler Toledo, d = 0.1 μg).

The electrochemical performances of full-cell devices were determined at an average mass loading amount of 3–4.5 mg cm⁻² for the total mass of anode and cathode materials.

**Assembly and Electrochemical Measurements of Full-Cell Devices:** Sodium-ion energy storage full cells were assembled using the NMTiO₂ composite as the anode and the NG as the cathode, respectively. The NG cathode was prepared in the same manner as the anode. The electrochemical analysis was carried out using the same method as in the half-cell. The electrochemical measurements of the NMTiO₂//NG full cells were carried out in an operating potential range of 1–3.8 V. The electrochemical performances of full-cell devices were determined on the mass loading of 3–12 mg cm⁻² for the total mass of anode and cathode electrodes. The overall cell energy/power densities were calculated based on the total mass of cathode and anode materials (Section S3, Supporting Information).

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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**Conflict of Interest**

The authors declare no conflict of interest.

**Keywords**

high energy density, hybrid sodium-ion energy storage, N-doped mesoporous structures, robust cycle stability, ultrafast charging

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