Hybrid Energy Storage of Ni(OH)$_2$-coated N-doped Graphene Aerogel//N-doped Graphene Aerogel for the Replacement of NiCd and NiMH Batteries

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Although Nickel–Cadmium (NiCd) and Nickel–metal hydride (NiMH) batteries have been widely used, their drawbacks including toxic Cd and expensive La alloy at the negative electrodes, low energy density (40–60 Wh/kg for NiCd and 140–300 Wh/L for NiMH), low power density (150 W/kg for NiCd and 1000 W/kg for NiMH), and low working potential (1.2 V) limit their applications. In this work, Cd and La alloy were replaced with N-doped reduced graphene oxide aerogel (N-rGO$_{ae}$) providing a hybrid energy storage (HES) having the battery and supercapacitor effects. The HES of Ni(OH)$_2$-coated N-rGO$_{ae}$//N-rGO$_{ae}$ provides 1.5 V, a specific energy of 146 Wh/kg, a maximum specific power of 7705 W/kg, and high capacity retention over 84.6% after 5000 cycles. The mass change at the positive electrode during charging/discharging is 8.5 $\mu$g cm$^{-2}$ owing to the insertion/desertion of solvated OH$^{-}$ into the $\alpha$-Ni(OH)$_2$-coated N-rGO$_{ae}$. At the negative electrode, the mass change of the solvated K$^+$, physically adsorbed/desorbed to the N-rGO$_{ae}$, is 7.5 $\mu$g cm$^{-2}$. In situ X-ray absorption spectroscopy (XAS) shows highly reversible redox reaction of $\alpha$-Ni(OH)$_2$. The as-fabricated device without using toxic Cd and expensive La alloy has a potential as a candidate of NiCd and NiMH.

Although the Nickel–Cadmium (NiCd) and Nickel–metal hydride (NiMH) batteries have been widely used, their drawbacks including toxic cadmium and expensive lanthanum alloy at the negative electrodes, low energy density (40–60 Wh/kg for NiCd and 140–300 Wh/L for NiMH), low power density (150 W/kg for NiCd and 1000 W/kg for NiMH), and low working potential (1.2 V) limit their applications in electric vehicles, laptops, and mobile phones when compared with Li-ion batteries$^{1,2}$. At the positive electrode, NiOOH and Ni(OH)$_2$ are used for NiCd and NiMH, respectively.

Recently Ni(OH)$_2$-based supercapacitors have also attracted a superior attention because of its high theoretical specific capacitance (2,082 F g$^{-1}$)$^{3,4}$, affordable price, abundant natural resources, and excellent environment compatibility$^{4}$. More interestingly, some previous work even reported the remarkably high specific capacitances of Ni(OH)$_2$-based supercapacitors, which are over its theoretical value$^{5-10}$. Generally, $\alpha$-Ni(OH)$_2$ and $\beta$-Ni(OH)$_2$ are the two common phases of Ni(OH)$_2$, which have been using as the supercapacitor electrodes$^{11}$. $\alpha$-Ni(OH)$_2$/$\gamma$-NiOOH redox couple can transform to $\beta$-Ni(OH)$_2$/$\beta$-NiOOH redox couple easily, which can lead to a specific capacitance decay$^{12,13}$. However, many $\beta$-Ni(OH)$_2$-based supercapacitors with great electrochemical performance have still been reported$^{14-17}$. As the results, it needs more understanding in the charge storage mechanism of Ni(OH)$_2$-based supercapacitors. It is also necessary to note here that there is a critic arguing that Ni(OH)$_2$ storing the charges via a phase transformation cannot be considered as the conventional supercapacitor.
materials\textsuperscript{18,19}. Our results here also show that Ni(OH)\textsubscript{2}-coated N-doped reduced graphene aerogel (N-rGO\textsubscript{ae}) mainly stores the electronic charge via a bulk redox reaction especially as very slow charging/discharging rates. Although the reaction mechanism of the Ni(OH)\textsubscript{2} itself follows the reversible reaction \textsuperscript{(1)}\textsuperscript{20,21}, the charge storage mechanism of Ni(OH)\textsubscript{2} composites e.g., Ni(OH)\textsubscript{2}/graphene is not yet clear.

\[ \alpha\text{-Ni(OH)}_{2} + \text{OH}^- \leftrightarrow \gamma\text{-NiOOH} + \text{H}_2\text{O} + e^- \] (1)

Note, the reaction (1) originally introduced by Bode et al.\textsuperscript{1,2} is well known in NiCd and NiMH batteries. For the Ni(OH)\textsubscript{2} supercapacitors, the theoretical specific capacitance of Ni(OH)\textsubscript{2} is based on the reaction (1). However, the electrochemical property of \(\alpha\text{-Ni(OH)}_{2}\) is still far lower than its theoretical value due to its insulating property, poor capacity retention and irreversible reaction\textsuperscript{22}. To overcome the drawbacks of the Ni(OH)\textsubscript{2}, it was produced on the conducting graphene sheets providing a specific energy of ca. 37 Wh kg\textsuperscript{-1}\textsuperscript{3}. In this research, \(\alpha\text{-Ni(OH)}_{2}\) is coated on N-rGO\textsubscript{ae} and used for the asymmetric energy storage (AES) of Ni(OH)\textsubscript{2}/N-rGO\textsubscript{ae}/N-rGO\textsubscript{ae} leading to high specific energy and power. This is because N-rGO\textsubscript{ae} has high electrical conductivity (2 \times 10\textsuperscript{3} S cm\textsuperscript{-1})\textsuperscript{23}, high ionic conductivity due to nitrogen- and oxygen-containing groups and high porosity, which is good for the diffusion of the electrolyte\textsuperscript{24,25}. The as-fabricated AES of the Ni(OH)\textsubscript{2}-coated N-rGO\textsubscript{ae}/N-rGO\textsubscript{ae} in a CR2016 coin cell can deliver a wide cell working potential up to 1.5 V and high specific energy and maximum specific power of 146 Wh kg\textsuperscript{-1} and 7705 W kg\textsuperscript{-1}, respectively.

In addition, the charge storage mechanisms of both \(\alpha\text{-Ni(OH)}_{2}\)-coated N-rGO\textsubscript{ae} and N-rGO\textsubscript{ae} are investigated in this work by means of \textit{in situ} X-ray absorption spectroscopy (XAS) and \textit{in situ} electrochemical quartz crystal microbalance (EQCM). The result shows that the AES of \(\alpha\text{-Ni(OH)}_{2}\)-coated N-rGO\textsubscript{ae}/N-rGO\textsubscript{ae} can store charges via both physical adsorption and redox reaction.

\textbf{Results and Discussion}

\textbf{Morphologies of the as-synthesised materials.} The morphology of the as-synthesized materials was investigated by Field Emission Scanning Electron Microscopy (FE-SEM). The 3D porous network structure of N-rGO\textsubscript{ae} was coated on flexible carbon fiber paper (CFP) substrate (see Fig. 1a) for which the N-rGO sheets are interconnected each other forming high porosity aerogel. Other physicochemical properties of the N-rGO\textsubscript{ae} were previously reported by our group elsewhere\textsuperscript{26,27}. An FE-SEM image of Ni(OH)\textsubscript{2} electrodeposited on the N-rGO\textsubscript{ae}/CFP shows that Ni(OH)\textsubscript{2} was fully loaded to the pores of the N-rGO\textsubscript{ae} and the Ni(OH)\textsubscript{2} nanoparticles

\begin{figure}[h]
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\caption{FE-SEM images of (a) N-rGO\textsubscript{ae} spray-coated on CFP, (b) Ni(OH)\textsubscript{2} electrodeposited on the N-rGO\textsubscript{ae}/CFP. TEM images of (c) N-rGO\textsubscript{ae} and (d) Ni(OH)\textsubscript{2} coated on N-rGO\textsubscript{ae}.}
\end{figure}
were subsequently coated on the top layer in Fig. 1b. Note, lower magnification FE-SEM images of CFP and the as-electrodeposited α-Ni(OH)2 on CFP are displayed in Figure S1a and b, respectively. In addition, a transmission electron microscopy (TEM) image of N-rGOae in Fig. 1c indicates a few layers of N-rGOae sheets forming the wrinkle structure confirming the framework structure of the aerogel. This structure can address the restacking issue typically found in 2D graphene or rGO nanosheets. The interconnected porous structure can also deliver large surface area and porosity as well as great electrical conductivity. A TEM image of Ni(OH)2-coated N-rGOae sheets in Fig. 1d displays the dark Ni(OH)2 particles with 25 nm in diameter dispersed on the N-rGOae layers. Note, XRD, Raman, and XPS of Ni(OH)2, N-rGOae and Ni(OH)2-N-rGOae are shown in Figures S2 and S3 of the Supporting Information.

**Charge storage mechanisms.** The charge-discharge mechanisms of the α-Ni(OH)2-N-rGOae and N-rGOae electrodes were investigated using the EQCM together with the CV technique. The CV of the α-Ni(OH)2-coated N-rGOae electrode is presented in Fig. 2a. The forward scan started from 0 to 0.6 V vs. Ag/AgCl for which an anodic peak occurs at 0.43 V vs. Ag/AgCl indicating that working voltage of ca. 0.6 V exhibits a most likely rectangular shape representing a good EDLC behavior of the α-Ni(OH)2-N-rGOae electrode. Note, the Ni K-edge XANES of the samples were recorded and compared with Ni2+ in aqueous Ni(OH)2 solutions30. The oxidation reaction of Ni(OH)2 with OH− providing γ-NiOOH, a water molecule, and an electron through the oxidation of solvated OH− ions into α-Ni(OH)2 interlayer separation. Also, the increasing Δm during the forward scan refers to the charging mechanism29. On the other hand, the backward scan (the discharging process) was swept back from 0.6 to 0 V vs. Ag/AgCl. The Δm of the electrode is reduced back to an original value, 0 μg cm−2 (see a black dash line in Fig. 2a) due to the full desorption of solvated OH−. It can be concluded from the EQCM/CV results that the charge storage mechanism of the α-Ni(OH)2-N-rGOae is based on the interaction chemistry especially at slow scan rates. α-Ni(OH)2-N-rGOae is then considered as the battery-type electrode material.

For the N-rGOae electrode, the CV and Δm vs. the applied potentials are shown in Fig. 2b. The CV with a working voltage of ca. 0.6 V exhibits a most likely rectangular shape representing a good EDLC behavior of the N-rGOae. Broad peaks also represent the redox reactions of N-containing groups26,27. For the charging process, the range of potential from 0 V to −0.6 V vs. Ag/AgCl was applied for which the Δm is decreased at a working window from 0 to −0.2 V vs. Ag/AgCl due to the desorption of ionic species initially adsorbed/absorbed when the electrode is immersed in the electrolytes without applying potential. This counter-ion desorption observed in this work is in good agreement with the new perspective charge storage mechanism recently proposed using in situ NMR29. At a potential range between −0.2 V and −0.6 V vs. Ag/AgCl, the Δm is rapidly increased to 7.5 μg cm−2 due to the adsorption/absorption of hydrated K+ within the active pores of N-rGOae.

To confirm the charge storage behavior of the as-prepared α-Ni(OH)2-N-rGOae electrode, the in situ XAS technique was performed with the chronocamperometry in 1 M KOH electrolyte during applying the potentials stepped from 0.0, 0.35, 0.5 and 0.6 V vs. Ag/AgCl and the following backward scan at the applied potentials from 0.6, 0.4, 0.18 to 0 V vs. Ag/AgCl. Note, the Ni K-edge XANES of the samples were recorded and compared with Ni foil (Ni0, 8333.00 eV), NiO (Ni4+, 8345.20 eV) and LaNiO3 (Ni3+, 8348.20 eV) standards30. In Fig. 3a and b, the Ni K-edge fluorescence energy of the Ni(OH)2-N-rGOae electrode charged at 0.0 V vs. Ag/AgCl is 8345.25 eV (Ni3+226) and the adsorption energy remains constant at −2.26 eV until 0.35 V vs. Ag/AgCl before increasing to the energy value of 8347.84 (Ni2+229) and 8348.00 eV (Ni4+279) when the charging potentials were applied to 0.5 and 0.6 V vs. Ag/AgCl, respectively. This is due to the oxidation reaction of Ni(OH)2 with OH− providing NiOOH. This result further confirms the EQCM results. For the discharging process, the Ni K-edge fluorescence energy of the Ni(OH)2-N-rGOae electrode discharged at 0.4 V vs. Ag/AgCl is 8347.84 eV (Ni2+276) and continues to stable at 8345.25 eV (Ni3+226) when discharged at 0.18 V and 0 V vs. Ag/AgCl. These results also confirm the reversible redox reaction of Ni(OH)2-N-rGOae.

**Hybrid energy storage of Ni(OH)2-N-rGOae/N-rGOae.** The as-fabricated Ni(OH)2-N-rGOae/N-rGOae AES can provide a wide working potential (See Fig. 4a), which is greater than all aqueous-based Ni(OH)2 symmetric supercapacitors3,9,31. Note, the total active material of the device is 4.0 mg consisting of 1.47 mg of Ni(OH)2-N-rGOae at the positive electrode and 2.53 mg of N-rGOae at the negative electrode. In addition, the CV...
Figure 3. (a) In situ high-resolution Ni K-edge fluorescence XAS spectra of the as-prepared Ni(OH)$_2$-N-rGO$_{ae}$ electrode and Ni standard compounds and (b) the oxidation states vs. $\Delta E$ (eV) of the Ni(OH)$_2$-N-rGO$_{ae}$ electrode during charging/discharging by a chronoamperometry method at different applied potentials vs. Ag/AgCl.

Figure 4. (a) CV curves at different scan rates, (b) specific capacitance vs. scan rate, (c) $b$-value vs. potential (V), (d) total capacitances at different scan rates, (e) GCD curves and (f) specific capacitance vs. applied currents of the Ni(OH)$_2$-N-rGO$_{ae}$/N-rGO$_{ae}$ AES. Note, the total active material of the device is 4.0 mg consisting of 1.47 mg of Ni(OH)$_2$-N-rGO$_{ae}$ at the positive electrode and 2.53 mg of N-rGO$_{ae}$ at the negative electrode.
shows the characteristics of the pseudocapacitors consisting of both capacitive and faradaic currents. The couple redox peaks are observed owing to the intercalation and deintercalation of the solvated OH\(^-\)\((H_2O)_n\) (where \(n \geq 1\)) \(^{32}\). Whilst, the capacitive current observed in the CVs is mostly due to the adsorption of hydrated K\(^+\) on the N-rGO anode surface. The cell specific capacitances of the AES device are 484.3, 324.4, 247.8, 211.4, 179.1, 150.8 and 140.4 F g\(^{-1}\) at 1, 5, 10, 25, 50, 75 and 100 mV s\(^{-1}\), respectively (Fig. 4b). From a power law, the \(b\) value was then calculated\(^{33}\), \(i = av^b\) where the current is represented as \(i\) and the scan rate is represented as \(v\). The adjustable parameters are expressed as \(a\) and \(b\). Typically, the \(b\) value is equal to 1.0 for non-diffusion-controlled surface capacitive (an EDLC-like electrochemical feature) and equal to 0.5 for diffusion-controlled redox reaction, which is a typical battery behavior\(^{19, 34}\). From the beginning, the \(b\) value of the cell device is almost amounted to 1 before dropping down to 0.86 (see Fig. 4c) indicating that the specific capacitances of the device are contributed from both diffusion-controlled battery-type behavior and capacitive effect. The capacitive and intercalation contribution fractions are shown in Fig. 4d. It is clearly observed that they are sensitive to scan rates. In addition to the CV results, GCD curves were carried out and shown in Fig. 4e for which the shapes of the charge and discharge curves imply good conductivity, excellent coulombic efficiency and high electrochemical reversibility of the AES. Besides, the calculated cell capacitances are 487.1, 441.1, 434.5 and 406.5 F g\(^{-1}\) at 1, 2, 3 and 4 A g\(^{-1}\), respectively (see Fig. 4f). The actual working potential window excluding the \(iR\) drop is ca. 1.5 V.

When compared with other previous report, the as-fabricated Ni(OH)\(_2\)-N-rGO anode//N-rGO anode AES exhibits significantly higher specific capacitance than other Ni(OH)\(_2\)-based asymmetric supercapacitors (see Table S1 of the Supporting Information).

The electrochemical impedance spectroscopy (EIS) of the as-fabricated AES was eventually performed by applying a sinusoidal signal of 10 mV amplitude from 1 mHz to 100 kHz. The bottom left-hand corner of the Nyquist plot in Fig. 5a shows a high frequency result for which 2.6 \(\Omega\) of the charge transfer resistance (\(R_{ct}\)) due to the redox reaction and 0.4 \(\Omega\) of the internal resistance (\(R_i\)) are observed. Note, the \(R_i\) here is rather small compared with the other previous work\(^{35}\). To further investigate the power efficiency of the as-fabricated AES, the relaxation time (\(\tau_0\)), which is the minimum time required for discharging the stored charges from the AES, was determined and shown in Fig. 5b. The smaller \(\tau_0\) represents the higher power efficiency of the AES\(^{36}\). The response of frequency (\(f_0\)), which is corresponding to the maximum point energy curve, is estimated to be at 1.26 Hz. The determined \(\tau_0\) which is equal to \(1/2 \pi f_0\) is 125.77 ms indicating that the as-fabricated AES can provide a quick discharging process and also substantially faster than other previous report\(^{35}\). Remarkably, the device can display a high specific energy of 146 Wh kg\(^{-1}\) at a specific power of 4687 W kg\(^{-1}\) with the remaining of 115 Wh Kg\(^{-1}\) at 7705 W kg\(^{-1}\) (Fig. 5c). The highest specific energy here is much greater than 77.8 Wh kg\(^{-1}\) of the asymmetric supercapacitor of the Ni(OH)\(_2\)-graphene;graphene\(^{4}\) and significantly higher than 35.7 Wh kg\(^{-1}\) of the amorphous Ni(OH)\(_2\) supercapacitor\(^{4}\). The as-fabricated AES provides high capacity retention over 84.61% after 5000 cycles (see Fig. 5d). This number is rather high when compared with NiCd and NiMH batteries and

![Figure 5. The electrochemical properties of the Ni(OH)\(_2\)-N-rGO anode//N-rGO anode AES: (a) Nyquist plot, (b) the plots of normalized power with the frequency, (c) maximum power density vs. energy density compared with some previous report\(^{34, 43, 44}\) and (d) the capacity retention over 5000 cycles at 1 A g\(^{-1}\).](image-url)
other Ni(OH)$_2$-based supercapacitors. As the result, the Ni(OH)$_2$-N-rGO ae is ideally suitable for many high power and energy applications.

**Ex situ evaluation of the AES device.** After the AES devices were electrochemically tested, ex situ measurements of the disassembled positive electrodes were carried out by XRD, FTIR, XAS and XPS. The XRD results in Fig. 6a can imply that α-Ni(OH)$_2$ on the positive electrode after tested begins to convert to β-Ni(OH)$_2$ after 3000 cycles. Additionally, XRD patterns of β-Ni(OH)$_2$ with the diffraction peaks (100), (101), and (110), are initially witnessed on the XRD patterns of the Ni(OH)$_2$-N-rGO ae after 3000 cycles. The calculated interlayer spacing is reduced from 7.00 Å (α-Ni(OH)$_2$, JCPDS 38–715) to 4.45 Å (β-Ni(OH)$_2$, JCPDS 14–0117). The less interlayer spacing can obstruct the diffusion of the OH$^-$ (H$_2$O)$_n$ (where $n \geq 1$) clusters to the Ni(OH)$_2$ layers. To further investigate the phase transformation of α-Ni(OH)$_2$ to β-Ni(OH)$_2$ after long cycling, the Ni(OH)$_2$-N-rGO ae electrodes after tested at 1000, 3000 and 5000 cycles were investigated by FTIR and XPS techniques (see FTIR in Fig. 6b and XPS in Figure S5). In addition, ex situ XAS was applied to investigate the oxidation number of Ni element in the positive electrodes of the AESs after 1000, 3000 and 5000 cycles. The XANES spectra and oxidation state for each sample are shown in Fig. 6c and d, respectively. The Ni K-edge XANES of the samples was recorded and compared with Ni foil (Ni$^{+0}$, 8333 eV), NiO (Ni$^{+2}$, 8345.20 eV) and LaNiO$_3$ (Ni$^{+3}$, 8348.20 eV) standards. The adsorption edge energy of Ni on the electrode and after tested for 1000, 3000, and 5000 cycles are 8345.25 eV (Ni$^{+2.25}$), 8345.84 eV (Ni$^{+2.28}$), and 8345.91 eV (Ni$^{+2.39}$), respectively. These results indicate that the Ni(OH)$_2$ phase begins to transform after 3000 cycles. After 5000 cycles, the phase of α-Ni(OH)$_2$ is completely changed to β-Ni(OH)$_2$. When the interlayer distance is decreased, the charge mechanism does no longer follow the reversible reaction (1) anymore, the β-Ni(OH)$_2$ phase will get oxidized and turned to β-NiOOH rather than γ-NiOOH (see Figure S6) leading to poor capacity retention typically detected in the α-Ni(OH)$_2$-based AESs. The reaction mechanism is shown in details in Figure S6 of the supporting information.

**Conclusions**

N-rGO ae was produced from GO through a hydrothermal reduction with hydrazine and coated on the CFP via a spray-coating technique. α-Ni(OH)$_2$ was coated on the N-rGO ae substrate by an electodeposition using a chronoamperometry at −0.9 V vs Ag/AgCl for 5 min. The charge storage mechanism of α-Ni(OH)$_2$-coated N-rGO ae was investigated by in situ EQCM and XAS. The mass change of the positive electrode during the

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**Figure 6.** (a) XRD patterns and (b) FTIR spectra of the Ni(OH)$_2$-N-rGO ae/CFP electrodes after charged/discharged as well as (c) ex situ high-resolution XAS spectra and (d) the oxidation states vs. ΔE (eV) of the Ni(OH)$_2$-N-rGO ae after 1000, 3000 and 5000 cycles as compared with the Ni standard compounds.
charging/discharging processes determined by the EQCM is about 8.5 μg cm⁻² owing to the insertion/desorption of solvated OH⁻ ions into the interlayer spacing of α-Ni(OH)₂. At the negative electrode, the EQCM shows that the mass change of the solvated K⁺ electrolytes, physically adsorbed/desorbed to the N-rGOae electrode via the EDLC mechanism, is 7.5 μg cm⁻² during the charging/discharging processes. The Ni oxidation state of the Ni(OH)₂-N-rGOae electrode after charged at 0.0 V vs. Ag/AgCl is +2.26 and remained stable at this oxidation state until 0.35 V vs. Ag/AgCl before oxidized to acrylic sheets, which are used as the materials of the electrochemical cell, has a dimension of 2 × 2 cm². The Pt wire and the reference electrode is the Ag/AgCl (3 M KCl). After electrodeposition process, the Ni oxidation state of the Ni(OH)₂-N-rGOae electrode is reduced back to +2.76 after discharged at 0.4 V vs. Ag/AgCl and +2.26 at 0 V vs. Ag/AgCl. These results show good reversible redox reaction of the Ni(OH)₂-N-rGOae electrode. A single coin-cell AES of Ni(OH)₂-N-rGOae/N-rGOae (CR2016) was assembled using a hydrolyzed polyethylene separator absorbed with 1 M KOH. The as-fabricated energy storage can provide a wide working voltage of 1.5 V with a high specific energy of 146 Wh kg⁻¹ and a maximum specific power of 7705 W kg⁻¹ with 84.61% capacity retention after 5000 cycles. Interestingly, after 3000 cycles, the α-Ni(OH)₂, which has a wide interlayer separation of 7.0 Å, was partially changed to β-Ni(OH)₂, which has a narrower interlayer separation of 4.45 Å. This leads to the capacity retention decay since the β-Ni(OH)₂ has too narrow interlayer spacing for the solvated electrolytes, OH⁻ (H₂O)n where n ≥ 1. This energy storage device has a potential to be used in high energy and power applications. Also, this device has a bright potential to replace the NiCd and NiMH technologies since we do not need toxic Cd and expensive La alloy at the negative electrode.

**Experimental Section**

**Synthesis of nitrogen-doped reduced graphene oxide (N-rGOae).** A hydrothermal reduction method was used to synthesize N-rGOae. Briefly, 3 mg/ml of GO from the modified Hummers method was prepared in Milli-Q water using ultrasonication for 30 min. 0.5 M hydrazine hydrate (N₂H₄, 80% Merck) was added to the mixture, and then the suspension was poured into a Teflon-lined autoclave and heated at 100 °C for 3 h. After naturally cooling down the autoclave to room temperature, a vacuum filtration is used to collect the N-rGO hydrogel. The as-fabricated N-rGO was left in Milli-Q water at 25 °C and the water was daily replaced for washing out the remaining of reducing agent. After that, the hydrogel was frozen at 0 °C for 24 h. Then, the frozen hydrogel was put in a freezing dryer to remove water at −55 °C for 72 h to form the final product N-rGOae. Next, a spray coating technique is applied using an airbrush with 0.3 mm of brush nozzle (Paasche Airbrush Company, USA) to coat the N-rGOae on the CFP (Carbon fiber paper) surface at 20 psi and room temperature. Finally, the electrode was dried in vacuum oven at 60 °C for 24 h. 

**Electrodeposition of nickel hydroxide (α-Ni(OH)₂) on N-rGOae electrode.** Firstly, α-Ni(OH)₂ was deposited on the N-rGOae-coated CFP substrate by applying −0.9 V vs. Ag/AgCl for 5 min through a chronoamperometry method using a Metrohm AUTOLAB potentiostat (PGSTAT 302 N made in Netherlands running NOVA version 1.10.3 software). The electrodeposition solution (60 ml) is 0.1 M nickel (II) nitrate hexahydrate (Ni(NO₃)₂·6H₂O, 97% QRec) in 0.5 M sodium nitrate (NaNO₃, 99.5% QRec). The counter electrode is the platinum wire and the reference electrode is the Ag/AgCl (3 M KCl). After electrodeposition process, the as-electrodeposited α-Ni(OH)₂ (0.97 mg) on the 0.5-mg N-rGOae-coated CFP substrate was rinsed 5 times using Milli-Q water before putting into a vacuum dryer at 50 °C overnight to dry off the samples.

**Material characterizations.** Field-emission scanning electron microscopy (FE-SEM, JSM-7001F (JEOL Ltd., Japan)) and transmission electron microscopy (TEM, JEM 1220 (JEOL Ltd., Japan)) were applied to study the morphology of the as-prepared materials. The structures of the materials were examined by X-ray diffraction (XRD, Bruker optics, Germany) using a monochromatic Cu Kα radiation (λ = 1.5405 nm), Fourier Transform Infrared Spectrometer (FT-IR, PerkinElmer Paragon 1000) and Raman spectroscopy (Senterra Dispersive Raman Microscope, Bruker) with an excitation wavelength of 532 nm. The chemical composition on the surface of the materials was characterized by X-ray photoelectron spectroscopy (XPS, Axis Ultra DLD, Kratos Analytical Ltd) with Al-K alpha radiation (hv = 14,866 eV). For X-ray absorption spectroscopy (XAS) measurement, Ni K-edge fluorescent XAS was performed at a beamline No. 5.2 at the Synchrotron Light Research Institute (Public Organization), Nakhon Ratchasima, Thailand. The Ge(220) double-crystal monochromator (energy range 3440–12100 eV) is used and a fluorescence mode with a 4-element silicon drift detector, which was placed 90° to the beam and 45° to the sample, is applied.

**Fabrication of AES and the electrochemical evaluation.** The AES was assembled of the negative and positive electrodes with a geometrical coin cell (CR2016). Hydrolyzed polyethylene (PE) film with a thickness of 25 μm, which was used as the separator, was soaked in 1 M KOH for 10 min before used. Then, the separator was inserted between the positive electrode (1.47-mg Ni(OH)₂-N-rGOae coated on CFP) and the negative electrode.
(2.53-mg N-rGO_{ae} coated on CFP). Finally, the coin cell was then assembled by pressing with a crimper machine at 100 psi. The charge storage mechanism was performed by the EQCM technique via a cyclic voltammetry (CV) combining with quartz crystal microbalance techniques of Au/TiO_{2}. The EQCM electrode was tested in atmospheric pressure and at room temperature (25 °C) using a three-electrode system; Ag/AgCl (3 M KCl in gel) as a reference electrode and Au spiral shape as a counter electrode. The electrochemical property of the as-fabricated supercapacitors was evaluated by CV, galvanostatic charge–discharge (GCD), and electrochemical impedance spectroscopy (EIS) using a Metrohm AUTOBAS potentiostat (PGSTAT 302 N) made in Netherlands running NOVA software (version 1.11).

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**Author Contributions**
M.S. conceived and designed this work and wrote the paper; P.S. carried out the experiment, and P.I., A.K. and T.P. performed XAS and EQCM. All authors participated in the analysis and discussion of the results.

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