Tailoring NiO Nanostructured Arrays by Sulfate Anions for Sodium-Ion Batteries

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In this contribution, a novel sulfate-ion-controlled synthesis is developed to fabricate freestanding nickel hydroxide nanoarrays on Ni substrate. As an inorganic morphology-controlled agent, SO\(_4^{2-}\) ions play a critical role in controlling the crystal growth and the nanoarray morphologies, by modulating the growth rate of adsorbed crystal facets or inserting into the metal hydroxide interlayers. By controlling the SO\(_4^{2-}\) concentration, the nanostructured arrays are tailored from one-dimensional (1D) Ni[SO\(_4\)\(_n\)]\(_m\)(OH)\(_{1-n}\) nanobelt arrays to hierarchical \(\beta\)-Ni(OH)\(_2\) nanosheet arrays. With further graphene oxide modification and postheat treatment, the obtained NiO/graphene hybrid nanoarrays show great potential for high-performance sodium-ion batteries, which exhibit a cyclability of 380 mAh g\(^{-1}\) after undergoing 100 cycles at 0.5 C and reach a rate capability of 335 mA h g\(^{-1}\) at 10 C.

1. Introduction

Sodium-ion batteries (SIBs) are promising low-cost alternative to current lithium-ion batteries (LIBs), considering the suitable redox potential (−2.71 V vs standard hydrogen electrode) and the sustainability advantages.[1] But the commonly utilized graphite anode for LIBs cannot function well in SIBs, due to the extremely low capacity and unfavorable thermodynamics.[1b] Therefore, numerous attempts have been made to explore high-performance anodes for SIBs, such as hard carbon, alloy-based, metal oxide, sulfide, and organic-based anodes.[1,2]

However, the radius of sodium ions (0.102 nm) is relatively larger than that of lithium ions (0.076 nm), resulting in severe volume expansion and low reaction kinetics of the anode materials.[2b,c] Fortunately, since the mechanical stability and sodium storage kinetics are related to the morphology and structure, nanostructure engineering and carbon hybridization of anode materials are highly desirable for SIBs.[2b,3] and the approaches to control the morphology and structure are fundamentally crucial.

Up to now, tremendous efforts have been invested in well-controlled synthesis of functional nanomaterials.[4] Two synthetic strategies are commonly used to control the dimensions and morphologies of nanostructured materials. One approach is by applying the templates (hard or soft template)[5] to physically control the dimensions and morphologies of the crystal grain growth, while the other is by applying appropriate additives (capping agent, surfactant, block copolymer, etc.)[6] to kinetically control the growth rate of specific crystal facets. However, the removal process of templates or organic additives is usually time and energy consuming, accompanied with the risk of introducing heterogeneous impurities. As a result, alternative approaches have been developed to control the morphology and structure with the help of inorganic species,[7] avoiding the complicated and consuming purification process. Hence, developing inorganic salts as the morphology-controlled agents is cost-effective, energy-saving, and environmentally friendly. Additionally, inorganic species usually perform as capping agents that selectively adsorb on specific crystal facets, resulting in anisotropic crystal growth and controlled morphologies.[7b,c,8]

Recently, it has been reported that various anions are able to insert into the interlayers of the layered hydroxides, leading to the novel hydroxides with different morphologies. The relative binding energies toward these interlayer anions in hydroxides follow the order: CO\(_3^{2-}\) > SO\(_4^{2-}\) > OH\(^-\) > F\(^-\) > Cl\(^-\) > Br\(^-\) > NO\(_3^-\).[9] As a divalent anion, sulfate ions (SO\(_4^{2-}\)) have higher affinity than the monovalent anions, which is more probable creating new complex compounds.[9] Moreover, SO\(_4^{2-}\) ions can influence the crystal growth remarkably when it is being adsorbed on the growing facets, owing to the steric hindrance effect[8b] and strong bridging-bidentate adsorption.[10] As a result, various metal hydroxysulfate (e.g., Ni[SO\(_4\)]\(_3\)(OH)\(_4\),[11] Cu[OH]SO\(_4\),[12] Co\(_x\)(OH)\(_y\)(SO\(_4\))\(_z\)(H\(_2\)O)\(_{4-x}\),[13] etc.) nanomaterials have been prepared as a family of layered hydroxides. Therefore, a systematic study on the effects of the SO\(_4^{2-}\) ions on the crystal growth habit and the nanomaterial morphology is necessary.

Herein, a sulfate-ion-controlled method is successfully developed to tailor the morphologies and structures of the
nickel hydroxide precursors for NiO nanoarrays. The synthesis approach is hydrothermally conducted in the nonalkaline aqueous solutions, containing NiSO₄ and Na₂SO₄ reagents with Ni foams as the substrates. Through controlling the concentration of sulfate ions during the reaction, different morphologies and structures from β-Ni(OH)₂ nanosheet arrays to Ni[SO₄]₀.₃(OH)₁.₄ nanobelt arrays are obtained. This controllability is attributed to the morphology-controlled effect of SO₄²⁻ ions, which selectively inhibit the growth rate of specific crystal facets or ions insertion into the interlayers of the nickel hydroxides. To explore the potential applications of these nanoarrays in SIBs, NiO/graphene hybrid arrays are prepared after graphene oxide decoration and postheat treatment. The hierarchical nanoarrays can suppress the restacking of graphene sheets and enable fast Na⁺ transportation. In addition, both graphene incorporation and arrayed structure can buffer the volume change and provide fast electron transport pathway, leading to a synergistic improvement of the electrochemical performance. When used as an anode in SIBs, the freestanding NiO/graphene nanoarrays exhibit superior cyclability (380 mA h g⁻¹ after 100th cycle at 0.5 C) and rate capability (335 mA h g⁻¹ at 10 C).

2. Results and Discussion

2.1. Sulfate-Ion-Controlled Synthesis of the Precursor Hydroxide Nanoarrays

In order to reveal the SO₄²⁻-controlled effects, various concentration of SO₄²⁻ ions during the reaction have been studied (Table S1, Supporting Information). To simplify the reaction system, NiSO₄ and Na₂SO₄ were chosen as the only reagents for the controlled experiments. Hydrothermal reactions were conducted in nonalkaline aqueous solutions, which contain 0.025 mol L⁻¹ of NiSO₄ with different concentration of Na₂SO₄. Figure 1a shows the powder X-ray diffraction (XRD) patterns of the obtained nanoarrays on nickel foams, which reflect the crystal phase transformations. As shown in Figure 1a, there are also two strong diffraction peaks (asterisks,* located at 44.5°...
arrays are densely grown on the substrate (Figure 1g and 14-0117). A large-scale coverage of the well-aligned nanosheet arrays of Na$_2$SO$_4$, changes into hexagonal phase, with further increasing the Na$_2$SO$_4$ to 4.0 mmol, the morphology of the nanobelt arrays shows the crystal phase changes from pure Ni(SO$_4$)$_{0.3}$(OH)$_{1.4}$ phase with cell parameters of $a = 7.89$ Å, $b = 2.96$ Å, $c = 13.63$ Å, and $\beta = 91.1^\circ$ (JCPDF No. 41-1424). A large-scale coverage of one-dimensional (1D) nanobelt arrays with good uniformity are grown on the nickel foam (Figure 1b). The well-defined belt-like structures have width of 200–500 nm and length up to several micrometers (Figure 1c). The transmission electron microscope (TEM) image in Figure S1 (Supporting Information) further confirms the typical nanobelt structure, which is consistent with the field emission scanning electron microscope (FESEM) observations (Figure 1b,c). The indexed area electron diffraction (SAED) pattern (see Figure S1, Supporting Information, inset) indicates the single-crystalline nature and the crystal growth along the [010] direction of the Ni(SO$_4$)$_{0.3}$(OH)$_{1.4}$ nanobelt.

Subsequently increasing the concentration of SO$_4^{2-}$ by adding extra Na$_2$SO$_4$ (1.0–3.0 mmol) into the NiSO$_4$ aqueous solution (10 mL, 0.025 mol L$^{-1}$), results in subtle and insignificant change in the morphology of the nanobelt arrays (Figure S2, Supporting Information), but the change of the crystal phase is observed. Figure S3 (Supporting Information) shows the crystal phase changes from pure Ni(SO$_4$)$_{0.3}$(OH)$_{1.4}$ phase (1.0 and 2.0 mmol of Na$_2$SO$_4$) to mixed phases of $\beta$-Ni(OH)$_2$ and Ni(SO$_4$)$_{0.3}$(OH)$_{1.4}$ (3.0 mmol of Na$_2$SO$_4$). But with further increasing the Na$_2$SO$_4$ to 4.0 mmol, the morphology becomes nanoplate arrays covered with a few nanobelts (Figure 1d), with only a little trace of Ni(SO$_4$)$_{0.3}$(OH)$_{1.4}$ phase existing in the sample as characterized in Figure 1a(2).

When the concentration of Na$_2$SO$_4$ is increased up to 5.0 mmol, Figure 1a(3) shows that the crystal phase completely changes into hexagonal $\beta$-Ni(OH)$_2$ phase (JCPDF No. 14-0117). As illustrated in Figure 1e and Figure S4a (Supporting Information), significant morphological change can be observed, which the hierarchical nanosheet arrays are decorated with quasi-hexagonal nanosheet subunits. A close observation reveals that the well-defined quasi-hexagonal subunits with a size range of 200–400 nm firmly attach on the supporting nanosheet surface (Figure 1f). TEM image as shown in Figure S4b (Supporting Information) further confirms the existence of these subunit structures, which is consistent with the FESEM observation. The SAED pattern (Figure S4b, Supporting Information, inset) indicates the crystalline symmetry along the [001] zone axis, from which the (110), (100), and (010) planes can be indexed.

As shown in Figure 1g–i, after greatly increasing the SO$_4^{2-}$ concentration by additionally adding 10.0 mmol of Na$_2$SO$_4$, $\beta$-Ni(OH)$_2$ nanosheet arrays decorated with numerous nanoparticles are successfully obtained. The XRD diffraction peaks at 19.2°, 33.0°, 38.5°, 59.0°, and 62.7° can be indexed to the hexagonal $\beta$-Ni(OH)$_2$ phase (see Figure 1a(4), JCPDF No. 14-0117). A large-scale coverage of the well-aligned nanosheet arrays are densely grown on the substrate (Figure 1g and Figure S5a, Supporting Information). A closer observation indicates that the nanosheets are decorated with numerous nanoparticles (Figure 1h), which are different from the detailed structure of the reported Ni(OH)$_2$ nanosheets.[14] TEM image in Figure 1i further confirms the supporting nanosheet surface is attached with numerous nanoparticle subunits. When zooming in to those subunit nanoparticles (dark spots), many surrounding bright features are also observed (Figure S5b, Supporting Information). This diffraction contrast possibly attributes to the irradiation damage under high-energy electron beam. This phenomenon has also been observed by other researchers,[7a,15] which is likely ascribed to the sensitivity of hydroxide species subjected to the electron-beam irradiation during TEM observations. The high-resolution TEM (HRTEM) image shown in Figure S5c (Supporting Information) further reveals there are defect sites (marked with red circles) dispersed between the discontinuous lattice fringes. The SAED pattern (the inset of Figure 1i) shows bright diffraction spots along the [001] zone axis, indicating the attached nanoparticle subunits have a relatively ordered orientation and it is the same with the supporting nanosheet.[15b]

The phase transition from Ni(SO$_4$)$_{0.3}$(OH)$_{1.4}$ to $\beta$-Ni(OH)$_2$ is further characterized by Raman measurements. Figure S6 (Supporting Information) shows the Raman spectra of the nickel-based hydroxide samples as discussed in Figure 1 and Figures S1–S5 (Supporting Information). As summarized in Table S1 (Supporting Information), Na$_2$SO$_4$ concentration of 0–2.0 mmol leads to pure Ni(SO$_4$)$_{0.3}$(OH)$_{1.4}$ phase, Na$_2$SO$_4$ concentration of 5.0–10.0 mmol leads to pure $\beta$-Ni(OH)$_2$ phase, and Na$_2$SO$_4$ concentration of 3.0 and 4.0 mmol leads to a mixed phase. When the concentration of Na$_2$SO$_4$ is 0.0, 1.0, or 2.0 mmol, pure Ni(SO$_4$)$_{0.3}$(OH)$_{1.4}$ phase shows three strong features located at 961, 984, and 1080 cm$^{-1}$ and two medium peaks at 484 and 607 cm$^{-1}$, which implies that sulfate ions might occupy two distinct chemical environments. The peaks observed at 607 and 984 cm$^{-1}$ are close to the positions of free sulfate ions (cf., 613 and 981 cm$^{-1}$, respectively),[16a-c] which can be attributed to some adsorbed sulfate species. The Raman bands observed at 484 and 1080 cm$^{-1}$ are similar to the positions of anion-intercalated $\alpha$-Ni(OH)$_2$ materials (cf., 495 and 1075 cm$^{-1}$, respectively)[16a,b] or its isostructural compounds (basic nickel hydroxyl sulfate salts)[16b] suggesting that sulfate ions are incorporated in the chemical environment.[16a] The peak identified at 961 cm$^{-1}$ might also related to the Ni(SO$_4$)$_{0.3}$(OH)$_{1.4}$ phase, which disappeared during increasing the Na$_2$SO$_4$ concentration, although it has not been previously reported. The peaks belonging to Ni(SO$_4$)$_{0.3}$(OH)$_{1.4}$ become less and less obvious when the Na$_2$SO$_4$ concentration is increased above 3.0 mmol. For samples of Na$_2$SO$_4$ concentration at 4.0 mmol, a new vibration at 525 cm$^{-1}$ appears, ascribing to a Ni$^2+$–OH translational lattice mode of $\beta$-Ni(OH)$_2$.[16a-d] For samples with Na$_2$SO$_4$ concentration is above 5.0 mmol, a new vibration at 311 cm$^{-1}$ emerges, which is assigned to the Ni$^2+$–OH rotational lattice vibrations ($E(R)$) of $\beta$-Ni(OH)$_2$.[16a,d] The Raman band at 447 cm$^{-1}$ also becomes more obvious, corresponding to the $A_{1g}$ lattice mode of $\beta$-Ni(OH)$_2$.[16a,b,d]

The results of Raman spectra are consistent with the phase transition trend as shown by the XRD studies (Figure 1a and Figure S3, Supporting Information).
2.2. Growth Mechanism of the Nanoarrays with the Help of SO$_4^{2-}$

On the one hand, the formation of nanoarrays on Ni substrates is ascribed to the extended self-sustained cycle of hydrolysis and etching (SCHE) method as described in our previous work,[11] which takes the advantages of the hydrolytic characteristics of metallic ions and the acid etched features of metal substrates. On the other hand, the different morphologies of the obtained nanoarrays are attributed to the morphology-controlled effect of sulfate ions (SO$_4^{2-}$), which selectively inhibit the growth rate of the adsorbed crystal facets or insert into the nickel hydroxide interlayers.

In order to observe the morphological and structural evolution during the Ni(SO$_4$)$_{0.3}$(OH)$_{1.4}$ nanoarray formation, time-dependent experiments were carried out in the NiSO$_4$ (0.025 mol L$^{-1}$) aqueous solutions without adding extra Na$_2$SO$_4$. The detailed formation process of the Ni(SO$_4$)$_{0.3}$(OH)$_{1.4}$ nanobelt arrays obtained at different time intervals was studied by XRD and FESEM, as shown in Figures S7 and S8 (Supporting Information), respectively. It is interesting to find that from the initial stage of 3 h, XRD pattern (Figure S7, Supporting Information) shows obvious diffraction peaks of the hexagonal β-Ni(OH)$_2$ phase (JCPDF No. 14-0117, denoted +), the corresponding FESEM images in Figure S8a,b (Supporting Information) present the nanosheet array morphology. These results are consistent with the early growth process of the β-Ni(OH)$_2$ nanosheet arrays obtained at the reaction time of 3 h. When increasing time to 4 h, the number of the diffraction peaks (Figure S7, Supporting Information) of the hexagonal β-Ni(OH)$_2$ phase decreased to two, indicating the β-Ni(OH)$_2$ phase might become less and less, but the traces of monoclinic Ni(SO$_4$)$_{0.3}$(OH)$_{1.4}$ phase (JCPDF No. 41-1424) are still hard to realize. As time increased to 5 h (Figure S7, Supporting Information), the Ni(SO$_4$)$_{0.3}$(OH)$_{1.4}$ phase starts to show its strongest diffraction peak (2θ = 40.2°). Further prolonging the reaction time, the pure Ni(SO$_4$)$_{0.3}$(OH)$_{1.4}$ phase can be obtained after reacting more than 6 h, the corresponding FESEM images in Figure S8c,d (Supporting Information) present an intermediate state nanosheet morphology.

Based on the above experimental results, it can be concluded that the hexagonal β-Ni(OH)$_2$ phase was first obtained in the initial stage according to the SCHE mechanism (Figure 2, the scheme). The hydrothermal hydrolysis of the Ni$^{2+}$ ions in a nonalkaline aqueous solution leads to the generation of nickel-based precursors and H$^+$ ions. Then nickel substrate was subsequently etched by the H$^+$ ions and meanwhile consumed the H$^+$ ions eventually. As a result, the consumption of H$^+$ ions in turn accelerated the hydrolysis of Ni$^{2+}$ ions, leading to a preferential growth of β-Ni(OH)$_2$ on the nickel substrate surface. At the same time, the Ni$^{3+}$ ions released from the Ni substrate supplemented the starting Ni$^{2+}$ ions in the solution, establishing a self-sustained hydrolysis, etching, and deposition cycle.

Following the above, the original β-Ni(OH)$_2$ nanosheet arrays transform into nanobelt arrays of monoclinic Ni(SO$_4$)$_{0.3}$(OH)$_{1.4}$ phase via “dissolution–crystallization” mechanism,[17] while change into β-Ni(OH)$_2$ hierarchical nanosheet arrays with the help of morphology-controlled SO$_4^{2-}$ ions, which is illustrated in Figure 2 (the scheme). The nanosheet or nanoparticle subunits on the supporting nanosheets are formed by secondary nucleation and growth on the surface of already existing nanosheets.[18] At the beginning of the nanoarray growth, the β-Ni(OH)$_2$ structural feature is in favor of rapid crystal growth along [100] and [010] direction to form plate-like structures. When the concentration of SO$_4^{2-}$ is relatively low, the sulfate ions prefer to insert into the interlayers of the nickel hydroxides. The amount of SO$_4^{2-}$ adsorbed on the (010) crystal facets of Ni(SO$_4$)$_{0.3}$(OH)$_{1.4}$ is lower on the (100) and (001) planes, leading to 1D structure growth along the [010] direction.[14b,19] This growth direction is consistent with the SAED observation in Figure S1 (Supporting Information, inset). Therefore, an appropriate range of SO$_4^{2-}$ concentration (e.g., 0.025–0.225 mol L$^{-1}$) under present experimental conditions could satisfy the demands of monoclinic Ni(SO$_4$)$_{0.3}$(OH)$_{1.4}$ anisotropic crystal growth, and result in the insertion of SO$_4^{2-}$ ions into the nickel hydroxide interlayers.

In contrast, a high SO$_4^{2-}$ concentration promotes not only the strong SO$_4^{2-}$ adsorption on the β-Ni(OH)$_2$ crystal facets perpendicular to the c-axis but also some SO$_4^{2-}$ adsorption perpendicular to the a- and b-axes. In our case, the β-Ni(OH)$_2$ quasi-hexagonal nanosheet subunits decorating on the supporting nanosheets were fabricated when the growth rates along the a-, b-, and c-axes were inhibited with different extent. When continuously increasing the SO$_4^{2-}$ (Na$_2$SO$_4$ up to 1.0 mol L$^{-1}$), the subunit crystals decorating on the supporting nanosheets became nanoparticles, because the inhibiting effect of the excessively SO$_4^{2-}$ adsorbed on different crystal facets tended to be the same. The higher concentration of SO$_4^{2-}$ ions has an inhibition effect on specific crystal planes just before the “dissolution–crystallization” formation of monoclinic Ni(SO$_4$)$_{0.3}$(OH)$_{1.4}$ nanobelt arrays. Finally, a conclusion can be
drawn from the intensive experiments on the growth process mentioned above. In most cases, the selective adsorption of additives on specific crystal planes can lower the surface energy and inhibit the growth along this direction. Different growth speed of the crystal planes results in anisotropic growth of the $\beta$-Ni(OH)$_2$ with different extent and finally leads to the products with different morphologies.

2.3. Characterization of NiO and NiO/Graphene Nanosheet Arrays

The Ni(SO$_4$)$_{0.3}$(OH)$_{1.4}$ nanobelt arrays and two hierarchical $\beta$-Ni(OH)$_2$ nanosheet arrays were calcinated at 400 °C for 2 h in a nitrogen atmosphere (Figures S9 and S10, Supporting Information, and Figure 3), for the purpose of measuring their electrochemical properties. The hierarchical nanosheet arrays with the morphology whose nanosheets’ surface is decorated with numerous nanoparticles, show a better SIB performance (Figure S11, Supporting Information). In order to better apply the nanosheet arrays as anode materials for SIBs, the $\beta$-Ni(OH)$_2$ hierarchical nanosheet arrays were incorporated with graphene oxides (GO). After thermal treatment in N$_2$ atmosphere, the NiO nanosheet arrays/graphene composite was obtained, which synergistically combines the freestanding nanoarrays and the high flexible graphene nanosheets with superior electrical conductivity.

As a consequence of postheating process at 400 °C for 2 h, the XRD patterns (Figure 3a) of the as-obtained NiO and NiO/graphene samples present the structural evolution from hexagonal $\beta$-Ni(OH)$_2$ to the monoclinic phase of NiO, with cell parameters of $a = 5.1101$ Å, $b = 2.9556$ Å, $c = 2.9512$ Å, and $\alpha = 90.0^\circ$, $\beta = 125.15^\circ$, $\gamma = 90.0^\circ$ (JCPDF No. 65-6920, space group: C2/m [No. 12]). The other two NiO nanoarrays derived from different precursors, which are prepared with 0.0 and 5.0 mmol of Na$_2$SO$_4$, show the similar XRD results (Figure S9, Supporting Information). The Raman spectra in Figure 3b show that the NiO/graphene sample has two characteristic vibrations observed at 1347 and 1583 cm$^{-1}$. The Raman peak located at around 1347 cm$^{-1}$ is usually derived from the K-point phonons of $A_{1g}$ symmetry mode of aromatic rings (the D band), and the vibration around 1583 cm$^{-1}$ could be attributed to the bond

![Figure 3](image_url)

Figure 3. a) XRD patterns, b) Raman spectra, c,d,f,g) FESEM, and e,h) TEM images of the hierarchical NiO (c–e) and NiO/graphene (f–h) nanosheet arrays obtained from thermal treatment of the $\beta$-Ni(OH)$_2$ precursors, which were prepared in the aqueous solution containing 0.25 mmol of NiSO$_4$ and 10.0 mmol of Na$_2$SO$_4$. 

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stretching of the \(E_{2g}\) symmetry mode of the sp\(^2\) carbon atoms (the G band).\[^{[21]}\] The intensity ratio of the D band and G band (\(I_D/I_G\)) is 1.16, indicating the disordered graphitic structures. The intense D band shown in the spectrum implies the formation of graphene lattice defects, which is related to the structure distortion of graphene layers to accommodate the surface geometry of the NiO nanosheet.\[^{[23]}\] In addition to the D band and G band, the peaks at about 388, 505, 715, and 1090 cm\(^{-1}\) are also observed, which correspond to the shaking vibration bands of NiO. The strong peaks at 505 and 1090 cm\(^{-1}\) are ascribed to the first-order (1LO) and second-order (2LO) scattering of the longitudinal optical phonon modes, while another two weak peaks around 388 and 715 cm\(^{-1}\) could be assigned to the first-order (1TO) and second-order (2TO) scattering of the transverse optical phonon modes of NiO.\[^{[23]}\]

The FESEM images (Figure 3c and Figure S10, Supporting Information) display the side view of the high yield of morphology-retentive NiO nanosheet arrays, which confirms that the freestanding nanosheet arrays are still firmly attached on the nickel foam after the decomposition of Ni(OH)\(_2\) into NiO. It can be seen that the hierarchical sheet-like architecture remains intact with numerous nanoparticle subunits firmly attached to the nanosheets (Figure 3d,g). So does the other two NiO nanoarrays derived from the precursors prepared with 0.0 and 5.0 mmol of Na\(_2\)SO\(_4\), the morphologies remained unchanged after thermal treatment process (Figure S9, Supporting Information). The SAED pattern in the inset of Figure 3e shows only several strong diffraction spots with partly polycrystalline features, from which the (111), (001), and (110) planes are indexed to the monoclinic NiO phase. The HRTEM image in Figure 3e (inset, down) shows well-resolved lattice fringes with spacings of 0.255 and 0.250 nm, corresponding to the (001) and (110) planes of monoclinic NiO, respectively. The top-view FESEM image in Figure 3f further confirms that a large scale of NiO/graphene nanosheet arrays are well aligned on the nickel foam. The TEM image in Figure 3h further provides evidence for the few-layer existence of graphene that enwrapped outside the NiO nanosheet. As shown in the figure, the clear coating layers of graphene with the lattice spacing of 0.347 nm are indexed to the (002) \(d\)-spacings of graphite, while the marked lattice fringes with spacings of 0.147 and 0.146 nm correspond to the (111) planes of monoclinic NiO.

Besides, thermal analysis is also conducted to investigate the graphene content in the NiO/graphene composite, which is calculated to be about 3.55 wt% as illustrated in Figure S12 (Supporting Information). The detailed analysis and calculation process has been described in the Supporting Information.

### 2.4. Electrochemical Performance for SIBs

Figure S11 (Supporting Information) presents the sodium storage performance for all of the three kinds of NiO nanoarrays. The nanosheet arrays decorated with nanoparticles show a relatively better SIB performance as they might have more electrochemical active sites for the energy storage application. Therefore, much attention and detail were dedicated to NiO hierarchical nanosheet arrays whose nanosheets’ surface is decorated with numerous nanoparticles.

Graphene-coated NiO nanosheet arrays with nanoparticle decoration were directly used as the anode electrodes for SIBs without using any binder or conductive agent. Electrochemical behaviors of the NiO/graphene nanosheet-array electrodes were evaluated by cyclic voltammetry (CV) and galvanostatic discharge–charge measurements. The CV test was carried out at a scan rate of 0.1 mV s\(^{-1}\) within the voltage range of 3.0–0 V versus Na/Na\(^+\) (Figure 4a). An intensive cathodic peak centered at 0.24 V with an unobvious shoulder aside (around 0.5 V) are identified in the first CV scan, which can be ascribed to the formation of solid electrolyte interphase (SEI) film and the reduction of NiO to metallic Ni.\[^{[3a,24]}\] Two anodic peaks around 0.51 and 1.60 V could be assigned to the partial decomposition of SEI film and the reoxidation of metallic Ni to NiO, respectively\[^{[3a]}\]. After the electrode activation of the first cycle, the shift of cathodic peaks to 0.56 and 1.01 V is observed during the subsequent cycles.

Figure 4b shows the initial five discharge–charge curves at a rate of 0.1 C between 0.01 and 3 V. The initial discharge/charge capacities are 940/595 mA h g\(^{-1}\), with an initial coulombic efficiency of about 63.3%. Then the discharge/charge capacities increase to 621 and 608 mA h g\(^{-1}\) at the fifth cycle after getting stabilized from the former cycles. Compared with the theoretical capacity of NiO (718 mA h g\(^{-1}\), based on a maximum
uptake of 2Na per NiO via the conversion reaction), the larger extra first discharge capacity is attributed to the electrolyte decomposition and subsequent formation of the SEI film on the surface of the electrode materials, which occurs in the low potential region.\(^{24b}\) An obvious potential plateau at around 0.5 V and a long potential slope at 0.42–0.01 V appear during the first discharge process. In the first charge curve, the corresponding plateaus near 0.4–0.5 and 1.5–1.9 V are observed. The subsequent discharge curves differ from the first one of which the plateaus shift upward. The changes of the potential range and the increase of charge capacity between the first and subsequent cycles are well consistent with the observation in the CV curves (Figure 4a).

Cycling performance of the NiO/graphene nanosheet arrays at current densities of 0.5 and 1.0 C is shown in Figure 4c. For comparison, the performance of pristine NiO nanosheet arrays without graphene coating was also measured. It can be observed that the NiO/graphene nanosheet arrays exhibit slower capacity fading and higher capacity retention than that of the pristine NiO nanosheet arrays. Besides, it can also be realized that the NiO/graphene nanosheet arrays showing lower specific capacities at the first ten cycles and then increasing until to a maximum value, leading to high capacity retentions for 100 cycles. This increase in specific capacity might be explained by the initial blockage of Na-ions due to the graphene coating, while the kinetics would be improved after several cycles of activation of Na-ions diffusion pathways and fully displayed discharge capacity can be obtained. The specific capacities of the NiO/graphene nanosheet arrays maintain at 380 and 321 mA h g\(^{-1}\) during the 100th cycle at a current density of 0.5 and 1.0 C, comparable to that of pristine NiO nanosheet arrays with 280 and 233 mA h g\(^{-1}\). Prolonged cycling performance of 200 cycles associated with the related coulombic efficiencies is shown in Figure S13a,b (Supporting Information).

Rate performances at various rates of the NiO/graphene and pristine NiO nanosheet arrays were also evaluated. As shown in Figure 4d and Figure S13c (Supporting Information), after first five cycles at 0.1 C for the electrode activation, the NiO/graphene nanosheet arrays exhibit relatively higher capacities at following current rates, which deliver an average capacity of 629, 543, 501, and 465 mA h g\(^{-1}\) at a current density of 0.1, 0.5, 1, and 2 C, respectively. When the current density further increases to 5 and 10 C, the NiO/graphene nanosheet arrays still retain an average discharge capacity of about 410 and 335 mA h g\(^{-1}\). While the pristine NiO nanosheet arrays deliver an average capacity of 625, 489, 436, 385, 311, and 227 mA h g\(^{-1}\) at a current density of 0.1, 0.5, 1, 2, 5, and 10 C, respectively. When the rate recovers to 0.1 C, the reversible capacity can increase back to 567 mA h g\(^{-1}\), suggesting that the NiO/graphene nanosheet-array electrode possesses excellent rate capability.

The electrochemical performance of the hierarchical NiO/graphene nanosheet arrays is comparable to the results reported in the related literatures.\(^{18a,24b,25}\) For example, NiO/Ni/graphene composites with hollow ball-in-ball nanostructure are obtained from Ni-based metal–organic frameworks, which exhibit about 200 mA h g\(^{-1}\) after 190 cycles at a current density of 1 A g\(^{-1}\) and the rate performance of 207 mA h g\(^{-1}\) at 2 A g\(^{-1}\) for SIBs.\(^{24b}\) In another recent work, core–shell NiO/carbon composites with NiO nanosheets growing on hollow carbon microspheres deliver a specific capacity of 309 mA h g\(^{-1}\) in the 50th cycle at a current density of 0.1 A g\(^{-1}\) and a rate performance of 183 mA h g\(^{-1}\) at 2 A g\(^{-1}\).\(^{25b}\) An earlier report shows that the ultrathin NiO nanosheets exhibit a specific capacity of 266 mA h g\(^{-1}\) during the 100th cycle at a current density of 1 A g\(^{-1}\) and a rate performance of 154 mA h g\(^{-1}\) at 10 A g\(^{-1}\) for SIBs.\(^{24b}\)

To investigate the charge transfer kinetics of the electrode materials, the electrochemical impedance spectroscopy (EIS) measurements are conducted. The resulting Nyquist plots of all the electrodes as shown in Figure S13d (Supporting Information) consist of a semicircle in the high-frequency range followed by an extended linear tail in the low-frequency region. In the high-frequency regions, the NiO/graphene nanoray electrode always features smaller semicircles before and after long-term cycling in comparison to that of the pristine NiO nanoray electrode, corresponding to a lower charge transfer resistance. According to the fitted equivalent circuit (inset of Figure S13d, Supporting Information), the charge transfer resistances (R\(_{ct}\)) of the two compared electrodes at different cycles are distinguished. The R\(_{ct}\) values for the NiO/graphene nanoray electrode before and after long-term cycling are 37.5 and 93.4 Ω. By contrast, the pristine NiO nanoray electrode before and after long-term cycling have bigger R\(_{ct}\) values, which are 64.9 and 109.9 Ω. The results indicate that the graphene wrapping on the arrayed structure can provide a continuous and fast pathway for electron transport.

To investigate the sodium-driven structural and morphological changes, the NiO/graphene and NiO electrodes of nanosheet arrays decorated with nanoparticles were collected and studied from the disassembled cells, which had undergone rate performance tests corresponding to Figure 4d. The cells were recharged to 3.0 V then disassembled, the electrodes were collected and washed with diethyl carbonate (DEC) and ethanol for several times. Figure S14 (Supporting Information) presents the FESEM images of the disassembled NiO/graphene and NiO nanosheet arrays after testing rate performance. The distinct outlines of the graphene-coated NiO nanosheet arrays have been better maintained, compared with the pristine NiO nanosheet arrays. The other two graphene-coated NiO nanoray electrodes, which are nanobelt arrays and nanosheet arrays decorated with hexagonal nanosheet subunits, are also tested rate performance and disassembled with the same procedure (Figure S15, Supporting Information). The 1D nanobelt structures and the hexagonal nanosheet subunits can still be identified, which maintain the arrayed morphology and attach on the current collectors. The results reveal that the graphene-coated nanoray structures are stable and can still be sustained after repeated phase conversion reactions.

The enhanced performances are attributed to the self-supported arrays directly constructed on the current-collecting substrate, as well as the highly conductive and flexible graphene nanosheets decorated on the nanostructured arrays. This attractive architecture takes the advantages of both nanostructured arrays and graphene-wrapped composites, thus providing more synergistic improvement.

On the one hand, the mechanically flexible graphene (serves as an elastic buffer) and the internal space within the
nanostructured arrays, both provide buffer for the volume change associated with the Na-ion insertion/extraction, thus sustaining the structural stability of electrode materials. The above results show that the few graphene layers encapsulated outside of the NiO nanosheets help maintain the capacities at high current rates. On the other hand, the nanostructured arrays have direct electronic pathways access to current collector, while the highly conductive graphene sheets (covering on the nanostructured arrays) form a unique 3D charge carrier transport network. Both can improve the conductivity and allow for faster electron transport, which is favorable for accelerating the electrochemical reaction kinetics. Besides, served as a robust scaffold/backbone, the nanostructured arrays effectively suppress the aggregation or restacking of graphene sheets[26] and maintain the excellent characteristics of the 2D materials. As a result, fully displayed discharge capacity, improved cycling stability, and enhanced high-rate performance are obtained at all rates of charging/discharging.

3. Conclusion

In summary, an inorganic-anion-controlled synthesis is successfully explored to fabricate the freestanding nickel hydroxide nanoarrays on Ni substrates. As a morphology-controlled agent, \( \text{SO}_4^{2-} \) ions play a crucial role in determining the morphologies and structures of the obtained nanoarrays by selectively inhibiting the growth rate of the crystal facets or entering the interlayers of the nickel hydroxides. Through controlling the concentration of \( \text{SO}_4^{2-} \), the nanoarrays can be tailored from 1D \( \beta\)-Ni(OH)\(_2\) nanobelt arrays to hierarchical \( \beta\)-Ni(OH)\(_2\) nanosheet arrays. With an appropriate \( \text{SO}_4^{2-} \) concentration, hierarchical \( \beta\)-Ni(OH)\(_2\) nanosheet arrays decorated with quasi-hexagonal nanosheet subunits or decorated with numerous nanopillars are obtained. After coating graphene oxide followed by the postheat treatment, the graphene/NiO hierarchical nanosheet arrays exhibit improved cyclability and rate capability when directly used as the anodes for SIBs. Both graphene incorporation and arrayed structure can buffer the volume change and allow for fast electron transport, besides the aggregation of graphene sheets is suppressed by nanoarrays, leading to a synergistic improvement of the electrochemical performance. As a result, a novel sulfate-ion-controlled synthesis is developed to fabricate specific functional materials.

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

morphology control, nanostructured arrays, nickel oxide, sodium-ion batteries, sulfate ions

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