General Polyethyleneimine-Mediated Synthesis of Ultrathin Hexagonal Co₃O₄ Nanosheets with Reactive Facets for Lithium-Ion Batteries

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Ultrathin hexagonal Co₃O₄ nanosheets with exposed reactive facets and porous architectures are synthesized by using a polyethyleneimine (PEI)-mediated hydrothermal strategy. Characterization of the material indicates typical Co₃O₄ nanosheets of hexagonal shape that are approximately 100 nm in side length and 15 nm thick. PEI plays crucial roles in the synthesis of hexagonal Co₃O₄. The effects of the reaction conditions on the precursor morphologies and dimensions are investigated to understand the various roles of PEI. Electrochemi-

cal tests reveal the superior performance of ultrathin hexagonal Co₃O₄ nanosheets, including a remarkable specific capacity (e.g. 1007 mAh g⁻¹ at 100 mA g⁻¹ and 858 mAh g⁻¹ at 500 mA g⁻¹), excellent cyclability (e.g. capacity retention: 96–99%), and a high rate capability. The improved performance is attributed to the combined effects from the high percentage reactive facets as well as the ultrathin and porous structures. This synthesis strategy can be extended to fabricate other anode materials for lithium-ion batteries.

1. Introduction

Rechargeable lithium-ion batteries, one of the most important portable power sources, have aroused considerable interest in recent years. Owing to their high energy density, improved efficiency, and lifetime, they have achieved great successes in many practical applications, such as portable electronics, hybrid electric vehicles (HEVs), and plug-in hybrid vehicles (PHEV).^[1–3] Currently, graphite (LiC₆, theoretical specific capacity: 372 mAh g⁻¹) is widely used as a conventional anode material for lithium-ion batteries.^[4] Nevertheless, a high specific capacity, high coulombic efficiency, and long cycling life are still highly desirable in anode materials for the advancements of lithium-ion batteries.^[5,6] Many significant efforts have been devoted to the development of high-capacity anode materials to

meet the growing demand for lithium-ion batteries with high energy and powder densities. Various novel anode materials, such as graphene nanoribbons, metal oxides, and metal sulfides, have been extensively explored for high-energy-density lithium-ion batteries.^[7–11]

Recently, transition-metal oxides (MO, where M is Co, Ni, Cu, or Fe) have been regarded as potential candidates for next-generation anode materials in lithium-ion batteries, because of their high specific capacity, capacity retention, and recharging rates.^[12] Among them, Co₃O₄ is considered one of the most promising transition-metal oxides, owing to its capability of reacting with eight Li⁺ ions per formula unit, delivering a high theoretical capacity of 890 mAh g⁻¹.^[13,14] Thus, the theoretical specific capacity of Co₃O₄ is almost 2–3 times as high as that of commercially used graphite.^[15,16] Nanostructured Co₃O₄ materials have drawn particular attention in lithium-ion battery research, owing to their unique properties for improving electron transport and lithium-ion diffusion during electrochemical processes. To achieve high-capacity anode materials, various interesting nanostructured anode materials have been designed in previous studies, such as nanowires,^[17,18] nanotubes,^[19] nanoboxes,^[20] nanomesh,^[21] nanoflowers,^[22] nanoneedles,^[23] nanocages,^[24–26] nanosheets,^[27,28] snowflake-shaped Co₃O₄,^[29] and so forth.

Generally, nanostructures with different exposed reactive facets show significant impacts on battery performances. For instance, Li and co-workers reported that Co₃O₄ nano-octahedrons with (111) planes showed better cycling and rate performances than nanocubes with (001) planes.^[30] Xu et al. reported that nano-sized Co₃O₄ octahedra enclosed within (111) facets could exhibit a charge capacity of 955.5 mAh g⁻¹ for up to 200 cycles without obvious capacity fading.^[31] In addition, Wang et al. reported that the dominant high-energy (112)

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facets in Co_3O_4 nanomesh delivered a higher capacity of 380 mAh g^{-1} at a high current density of 1000 mA g^{-1} , as compared to conventional (111) and (100) planes.^[21] Previous work also indicated that 1.875 Co^{2+} and 1 Co^{2+} ions were found in (111) and (001) crystal facets, respectively.^[25] The high population of cobalt ions on the (111) facets enables fast electrochemical reactions between Co_3O_4 and Li^+ in the lithiation–delithiation process. Thus, synthesizing Co_3O_4 with exposed reactive facets is desirable for lithium-ion battery applications. Similar to other high-capacity anode materials, Co_3O_4 also suffers from huge volume expansion and severe particle aggregation during charge–discharge cycles, thus leading to large irreversible capacity loss, poor cycling stability caused by electrode pulverization, and loss of electronic contact with current collectors. The presence of a porous architecture in Co_3O_4 (e.g. nanoboxes, nanomesh, and nanocages) is confirmed to be beneficial for alleviating the pulverization problem of electrode materials^[20, 21, 24–26].

Until now, in the pursuit of high capacity anode materials, synthesizing nanostructured Co_3O_4 , particularly that with hexagonal nanostructures and reactive facets, has received tremendous attention. The unique nanostructure of Co_3O_4 can be directly inherited from corresponding metal-hydroxide precursors through heat treatment. By virtue of the interaction between certain organic molecules and inorganic crystal facets, Hou et al. used poly(vinylpyrrolidone) as a morphology-controlling agent for the formation of hexagonal $\text{Co}(\text{OH})_2$ nanoplatelets in a mixed solvent.^[32] In addition, Xiong et al. fabricated hexagonal $\text{Co}(\text{OH})_2$ nanosheets with a mixture of H_2O and ethanolamine by using a solvothermal method.^[33] However, when ethanolamine was replaced with diethanolamine, triethanolamine, and ammonia in the synthesis, only irregular products were obtained.^[33] So far, applicable structure-directing agents are still limited for the synthesis of hexagonal Co_3O_4 and the use of organic solvents can increase production cost and environmental burden. Recently, Zhan introduced $\text{Co}(\text{OH})_2$ hexagonal nanoplates through the hydrothermal treatment of CoCl_2 and NaOH without any templates or surfactants.^[34] Similarly, Su et al. employed a hydrothermal route to synthesize hexagonal $\text{Co}(\text{OH})_2$ nanosheets with CoCl_2 as the cobalt source and Na_2SO_4 as an additive.^[35] Nevertheless, these approach requires specific raw materials (ca. CoCl_2) and cannot easily be extended to different metal salts. Therefore, it is highly desirable, but challenging, to explore a general route for synthesizing porous hexagonal materials with exposed reactive facets to enhance the lithium-storage capacity.

In this study, ultrathin Co_3O_4 nanosheets endowed with (111) reactive facets are successfully synthesized by using a polyethyleneimine (PEI)-mediated hydrothermal treatment, followed by heat treatment in air. The as-prepared Co_3O_4 materials shows a hexagonal structure with a side length of about 100 nm and a thickness of 15 nm. Owing to the unique features, ultrathin hexagonal Co_3O_4 nanosheets exhibit a high specific capacity, good cycling stability, and excellent rate capability when tested in a half-cell. In comparison with pristine Co_3O_4 and thick Co_3O_4 nanosheets, the improved battery performance of ultrathin Co_3O_4 nanosheets is ascribed to the combined effects

from the porous ultrathin nanosheet structure and the (111) reactive facets. Thus, our results demonstrate the promising application of ultrathin hexagonal Co_3O_4 nanosheets with reactive facets as high-capacity anode materials in lithium-ion batteries. To the best of our knowledge, it is the first report on the PEI-mediated synthesis of ultrathin hexagonal Co_3O_4 nanosheets. Importantly, the PEI-mediated hydrothermal synthesis strategy proposed in this study has great potential to be extended to fabricate other metal-oxide-based anode materials (e.g. manganese- and nickel-based metal oxides) for lithium-ion batteries.

2. Results and Discussion

Figure 1 shows typical X-ray diffraction (XRD) patterns of the as-prepared precursors and final products. The XRD pattern of

Figure 1. XRD patterns of the $\text{Co}(\text{OH})_2$ precursors prepared by using the hydrothermal method and the Co_3O_4 products after subsequent heat treatment in air.

the as-prepared precursor (CNS-1P) reveals the formation of $\beta\text{-Co}(\text{OH})_2$, which is in good agreement with the literature values (JCPDS No. 30-0443). This is attributed to the precipitation reaction between cobalt ions and hydroxyl ions in the mixed solution. In contrast, all diffraction peaks of the final products (CNS-1) can be assigned to pure cubic phase of Co_3O_4 , consistent with standard cards (JCPDS No. 42-1467). No peaks from impurities [e.g. CoO , Co_2O_3 , and $\text{Co}(\text{OH})_2$] can be found, signifying high purity and crystallinity of Co_3O_4 in the final products. This can be explained by the dehydration, decomposition, and oxidation reactions of $\text{Co}(\text{OH})_2$ precursors in air under heat treatment at 400°C . A previous study stated that the conversion from $\text{Co}(\text{OH})_2$ to Co_3O_4 was known as a topotactic transformation.^[19] By using the Scherrer equation, the crystallite sizes of $\text{Co}(\text{OH})_2$ and Co_3O_4 are determined to be about 20 and 16 nm, respectively, confirming that heat treatment at 400°C does not significantly increase the crystallite size. The inhibition of crystallite-size growth is probably ascribed to the presence of PEI on the $\text{Co}(\text{OH})_2$ surface.

Figure 2. Typical FESEM images of the as-prepared Co(OH)_2 and Co_3O_4 : a, b) hexagonal Co(OH)_2 precursors and c, d) hexagonal Co_3O_4 products.

Figure 2 displays typical field-emission scanning electron microscopy (FESEM) images of Co(OH)_2 precursors (CNS-1P) synthesized through the PEI-mediated hydrothermal method and Co_3O_4 products (CNS-1) obtained upon subsequent heat treatment at 400°C . As shown in Figures 2a and 2b, the morphology of Co(OH)_2 without heat treatment is observed to have a well-defined hexagonal shape with sharp corners and edges. As shown in Figures 2c and 2d, the hexagonal nanosheets are around 100 nm in size and 15 nm in thickness. The slight size variation is probably caused by the non-uniform concentration distribution of reactants in our static hydrothermal synthesis, which might give rise to different crystal growth rates. Recently, a stirring hydrothermal route, which enabled a significant improvement in reactant diffusion, exhibited great potentials to be applied to PEI-mediated general synthesis for achieving uniform products.^[36] Heat treatment leads to the formation of many pores from a few to tens of nanometers in Co_3O_4 nanosheets, whereas the hexagonal nanosheet morphologies and dimensions are well maintained. The porous structures are formed in the products, probably owing to the dehydration of precursors and crystalline transformation during heat treatment. PEI should play crucial roles in the formation of precursors with a perfect hexagonal shape. When the hydrothermal synthesis is performed without PEI, irregular structures of Co_3O_4 (CNS-9) are found after heat treatment (Figure S1 in the Supporting Information). It is believed that the branched structures and long chains in the PEI molecules have unique functions in the formation of hexagonal shapes.

The microstructures of as-prepared Co(OH)_2 (CNS-1P) and Co_3O_4 (CNS-1) were further analyzed by using transmission electron microscopy (TEM). As shown in Figure 3, the hexagonal shapes of the precursors and products with high crystallinity can also be clearly seen, which is consistent with the FESEM analysis. The internal angles of precursors and products are determined to be about 120° . Pore sizes of about 5 and 57 nm are marked with arrows in the final products. As suggested in previous studies, the formation of pores in the center of the ul-

Figure 3. Typical TEM images of the as-prepared Co(OH)_2 and Co_3O_4 : a, b) hexagonal Co(OH)_2 nanosheets, c, d, f) porous hexagonal Co_3O_4 nanosheets, and e) single-crystal SAED pattern.

trathin hexagonal Co_3O_4 nanosheets could probably be attributed to the Kirkendall effect.^[37,38] The porous interior was attributed to the difference in oxidation rate and oxygen diffusion kinetics.^[37,38] The presence of multiscale pores in active electrode materials are beneficial for alleviating the volume variation problems in the charge–discharge process and enhancing the diffusion of Li-containing electrolyte to the active electrode. The selected-area electron diffraction (SAED) pattern in Figure 3e presents a regular hexagonal distribution, suggesting the single-crystal nature of Co_3O_4 . The diffraction spots can be well indexed as $(0, \bar{2}, 2)$, $(2, 0, \bar{2})$ and $(2, \bar{2}, 0)$ crystal planes with a d spacing of 0.28 nm and interfacial angle of 60° . The zone axis of the Co_3O_4 SAED pattern is confirmed to be $[111]$, indicating that the as-prepared porous Co_3O_4 nanosheets are predominately exposed with (111) facets. The percentage of (111) facets in the hexagonal Co_3O_4 nanosheets is determined to be about 85%. A previous study suggested that the formation of (111) facets of Co_3O_4 could be attributed to the close d spacing of the (001) facets of Co(OH)_2 .^[39] As shown in Figures 3b and 3f, the lattice d spacing values are 0.275 nm and 0.28 nm, which can be attributed to the (100) plane of Co(OH)_2

and the (110) plane of Co_3O_4 phase, respectively. The difference between the (100) facets of $\text{Co}(\text{OH})_2$ and the (111) facets of Co_3O_4 is about 1.8%. Thus, the well-defined lattice fringes confirm the crystalline structures and topotactic transition of the as-prepared $\text{Co}(\text{OH})_2$ and Co_3O_4 . Zhu et al. suggested that the arrangement of Co^{2+} in Co_3O_4 (111) facets was similar to that of Co^{2+} in $\text{Co}(\text{OH})_2$ (001) facets.^[40] The similarity of the lattice match and the Co^{2+} atomic arrangement are favorable for synthesizing Co_3O_4 with exposed (111) facets from (001)-dominated $\text{Co}(\text{OH})_2$ nanosheets through a topotactic transition. The energy-dispersive X-ray spectroscopy (EDS) analysis shows the presence of Co, O, C, and Cu in the precursors and final products (Figure S2). The existence of Cu and C is attributed to the carbon-coated copper grid used during the TEM analysis. This further confirms the presence of Co and O in the precursors and final products, which is in good agreement with the XRD analysis.

Thermogravimetric (TGA) and derivative thermogravimetric (DTG) analysis are useful techniques for understanding the thermal conversion of $\text{Co}(\text{OH})_2$ to Co_3O_4 . Figure 4 presents typi-

Figure 4. TGA and DTG curves of the as-prepared $\text{Co}(\text{OH})_2$ precursors and Co_3O_4 tested in an air atmosphere.

cal TGA and DTG results of $\text{Co}(\text{OH})_2$ precursors (CNS-1P) and Co_3O_4 nanosheets (CNS-1). For the $\text{Co}(\text{OH})_2$ precursors, the initial weight loss of 0.9 wt% at temperatures up to 100 °C can be ascribed to the evaporation of absorbed/trapped water molecules. With the increase in temperature, a significant weight loss 13.8 wt% was found for the precursors around 195 °C, as indicated by the DTG curve. This could be attributed to the phase transformation from $\text{Co}(\text{OH})_2$ to Co_3O_4 in an air atmosphere, as suggested by Equation (1).^[41] The experimental weight loss at this stage is close to the theoretical weight loss (13.6 wt%). No considerable weight loss was observed when the temperature was above 400 °C. It should be mentioned that the as-prepared Co_3O_4 material treated at 400 °C exhibits excellent thermal stability up to 800 °C, as indicated by the small weight loss (1.3 wt%). Also, TGA and DTG curves of PEI (Figure S3) measured in an air atmosphere suggest that the de-

composition of PEI is completed when the temperature is higher than 400 °C, implying that 400 °C is sufficient for the removal of PEI from Co_3O_4 :

The functional groups in the precursors and products can unveil the roles of PEI in the hydrothermal synthesis. Figure 5

Figure 5. FTIR spectra of the as-prepared $\text{Co}(\text{OH})_2$ precursors and Co_3O_4 .

depicts Fourier-transform infrared (FTIR) spectra of $\text{Co}(\text{OH})_2$ precursors (CNS-1P) and ultrathin Co_3O_4 nanosheets (CNS-1). For porous Co_3O_4 nanosheets, the presence of two sharp peaks at 577 and 670 cm^{-1} could be assigned to stretching vibrations of metal–oxygen bonds from Co_3O_4 .^[42] For $\text{Co}(\text{OH})_2$ precursors, the distinct peak at 3620 cm^{-1} is attributed to non-hydrogen-bond O–H stretching vibrations of $\text{Co}(\text{OH})_2$.^[43] This implies the complete conversion of $\text{Co}(\text{OH})_2$ to Co_3O_4 through thermal treatment in air, which is consistent with the XRD analysis. In addition, the peaks at 1630 cm^{-1} for $\text{Co}(\text{OH})_2$ precursors and porous Co_3O_4 nanosheets are ascribed to $-\text{NH}_2$ groups and bending vibrations of physically adsorbed H_2O , respectively.^[44] In these two samples, peaks located at 2930 and 2850 cm^{-1} could be attributed to $-\text{CH}_2-$ groups, and the peak at 1126 cm^{-1} could be ascribed to the stretching vibration of C–N bonds.^[44] For $\text{Co}(\text{OH})_2$ precursors, the $-\text{CH}_2-$ and C–N groups are from the PEI molecules. However, as suggested by the TGA data in Figure S3, it is believed that PEI was decomposed into carbon- and/or nitrogen-containing species by reaction with air at 400 °C. It is likely that these species could be adsorbed on the Co_3O_4 surface. Thus, the presence of $-\text{CH}_2-$ and C–N groups in Co_3O_4 (CNS-1), as detected by FTIR, should be attributed to the decomposition products of PEI, rather than PEI molecules. The broad peak at 3435 cm^{-1} is attributed to hydrogen-bonded water in $\text{Co}(\text{OH})_2$ and Co_3O_4 . Thus, FTIR analysis implies that PEI can be strongly adsorbed onto the precursor surface and play a role as morphology-directing agents for the hexagonal structure.

Figure 6. XPS analysis of the as-prepared Co(OH)_2 precursors and Co_3O_4 products: a) Co 2p, b) O 1s, c) N 1s, and d) C 1s.

Figure 6 shows the high-resolution X-ray photoelectron spectroscopy (XPS) analysis of the Co(OH)_2 precursors (CNS-1P) and Co_3O_4 product (CNS-1). The XPS survey scan verifies the presence of Co, O, and C in these two samples (Figure S4), which is consistent with the EDS analysis. As shown in Figure 6a, the high-resolution XPS spectrum of Co 2p of the final product indicates two major peaks located at 794.9 and 779.7 eV with a spin energy separation of 15.2 eV, indicating the typical $\text{Co}2p_{1/2}$ and $\text{Co}2p_{3/2}$ orbitals of Co_3O_4 . The $\text{Co}2p_{3/2}$ peak at 779.7 eV can be deconvoluted into two peaks at 780.6 and 779.4 eV, suggesting the coexistence of Co^{2+} and Co^{3+} species (e.g. CoO and Co_2O_3). The peak area ratio of Co^{2+} to Co^{3+} is determined to be 2.08, which is in good agreement with the theoretical value of 2 in Co_3O_4 . Co 2p XPS analysis of the precursors implies that the oxidation state of Co is +2, as suggested by the peak located at approximately 794.6 eV. It should be noted that two satellite peaks are also found at 802.6 and 786.8 eV, which further confirms that the oxidation of Co is +2 in the precursors. This means that no oxidation reactions occur during the hydrothermal process. As shown in Figure 6b, the O 1s peak confirms both lattice oxygen (binding energy, BE = 528.8 eV) and surface oxygen in hydroxyl groups

(BE = 531.0 eV) in the product, whereas oxygen species, mainly in the form of hydroxyl groups, are found in the precursors. As seen in Figure 6c, high-resolution N 1s analysis indicates the presence of nitrogen species in the precursors. Even though precursors are thoroughly washed with water and ethanol, a strong interaction between PEI and Co(OH)_2 is suggested by the XPS analysis, which is consistent with the FTIR analysis. Compared with the FTIR data, no nitrogen element was detected in Co_3O_4 (CNS-1) by using XPS, which can probably be attributed to the sampling depth of only a few nanometers. Previous work suggested that PEI adopted a high positive charge that was provided by the nitrogen atoms.^[45] Thus, the positively charged PEI molecules have a strong affinity to precursor surface through the electrostatic interaction between the amino groups of PEI and the $-\text{OH}$ group of the Co(OH)_2 surface. However, after heat treatment at 400 °C, no nitrogen species can be found in the Co_3O_4 products, owing to the complete decomposition of PEI in air at 400 °C. As indicated in Figure 6d, a unique peak at 287.2 eV can be attributed to the presence of C–O bonds in the Co_3O_4 products, owing to the adsorbed by-products from thermal decomposition of PEI.

Figure 7. Nitrogen adsorption isotherms and pore-size distribution of porous hexagonal Co_3O_4 nanosheets.

Figure 7 indicates the nitrogen adsorption–desorption isotherm and the Barrett–Joyner–Halenda (BJH) pore-size distribution of ultrathin Co_3O_4 nanosheets (CNS-1) treated at 400°C . The porous structure and high specific surface of the Co_3O_4 nanosheets are confirmed by the nitrogen adsorption–desorption isotherm at 77 K. The isotherms are of type IV with a hysteresis loop at high relative pressure (P/P^0), implying the presence of mesopores. The multipoint Brunauer–Emmett–Teller (BET) specific surface area of the Co_3O_4 nanosheets is about $32.4\text{ m}^2\text{ g}^{-1}$, which is comparable with hierarchical star-like Co_3O_4 ($25\text{ m}^2\text{ g}^{-1}$), porous Co_3O_4 nanoplate ($28.4\text{ m}^2\text{ g}^{-1}$), and Co_3O_4 nanobundles ($26.4\text{ m}^2\text{ g}^{-1}$)^[6,46,47] The high specific surface area is attributed to the anisotropic shape of ultrathin Co_3O_4 nanosheets and the porous structure. Both opposite-side surfaces and the six adjacent edges can contribute to the total surface area.^[48] In addition, the pore-size distribution curve (inset, Figure 7) based on the BJH method indicates that Co_3O_4 nanosheets show a bimodal nature with a narrow distribution centered around 2.7 and 52 nm, which is in good agreement with the TEM analysis (Figure 3). The formation of large pores is probably ascribed to the merging of numerous interconnected small pores under the thermal treatment. Previous work has suggested that porous nanostructures could substantially mitigate the mechanical strain from volume expansion and enhance the diffusion of a Li-containing electrolyte to active materials during the charge–discharge process, thus improving the cycling performance of electrode materials.^[49] Therefore, the high specific surface area and multiscale pore-size distributions of anode materials in this work are favorable for high-performance lithium-ion batteries.

Figure 8 illustrates the formation of the ultrathin Co_3O_4 nanosheets and the roles of PEI in the Co_3O_4 synthesis. It is believed that PEI plays important roles in the synthesis of ultrathin Co_3O_4 nanosheets through hydrothermal treatment and subsequent heat treatment. Firstly, when PEI is mixed with cobalt acetate, PEI is considered as the complexing agent to form PEI–cobalt intermediates. The cobalt ions, which have

Figure 8. Schematic illustration of the formation of ultrathin Co_3O_4 nanosheets and the roles of PEI in the hydrothermal synthesis: a) photo of cobalt acetate solution; b) photo of Co–PEI complex solution; c) reactant solution before hydrothermal treatment; d) photo of $\text{Co}(\text{OH})_2$ precursors; e) photo of Co_3O_4 final products; f) molecular structure of PEI; g) proposed Co–PEI complex, formed through interactions between the nitrogen atoms of PEI and cobalt ions.

empty valence-shell orbitals, can accept pairs of nonbonding electrons from nitrogen-containing groups (e.g. $-\text{NH}_2$, $\text{N}\equiv$, $-\text{NH}-$) in PEI to form covalent cobalt–nitrogen bonds, as illustrated in Figure 8 g. Previous studies have also reported that PEI can be used as a chelating agent with metal ions such as copper (II), nickel (II), and cobalt (II).^[50] Thus, when NaOH is added to the mixed solution, the growth kinetics of $\text{Co}(\text{OH})_2$ precursors through the precipitation reaction are modulated by gradually releasing cobalt ions during the dissociation of the PEI–cobalt complex. Secondly, PEI is generally regarded as a useful polycation, and one of the important features is the high concentration of positively charged nitrogen atoms.^[51] Therefore, PEI can selectively adsorb onto the crystal facets of negatively charged $\text{Co}(\text{OH})_2$ precursors under alkaline conditions, owing to the charge interactions. Similar anisotropic growth has been reported in ZnS capped by cysteine and Co_3O_4 nanosheets with hexamethylenetetramine.^[52,53] Thirdly, PEI is also beneficial in maintaining the particle size and material morphology during the thermal conversion from $\text{Co}(\text{OH})_2$ to Co_3O_4 under heat treatment in air. This can be used to explain the close dimensions and similar morphologies for $\text{Co}(\text{OH})_2$ and Co_3O_4 , as confirmed by FESEM, TEM, and XRD analysis.

To further understand the roles of PEI in the $\text{Co}(\text{OH})_2$ precursor synthesis, the effects of cobalt-salt type, amount of PEI, and reaction duration on the $\text{Co}(\text{OH})_2$ morphology and dimensions were systematically investigated. When cobalt acetylacetonate (CNS-2P), cobalt nitrate (CNS-3P), or cobalt sulfate (CNS-4P) are used in the hydrothermal synthesis, well-defined hexagonal $\text{Co}(\text{OH})_2$ nanosheets can still be found in the products (Figure S5). This indicates that PEI, rather than anions (e.g. CH_3COO^- , SO_4^{2-} , NO_3^- , etc.) from the metal salts, is the morphology-controlling agent for the formation of hexagonal $\text{Co}(\text{OH})_2$. This further signifies the crucial roles of PEI in the formation of hexagonal nanostructures.

However, Li et al. reported nitrilotriacetic acid as ligands to fabricate porous Co_3O_4 nanowires by using cobalt chloride as a starting material.^[54] When different metal salts (e.g. cobalt acetate and cobalt nitrate) were used in the material synthesis, only irregular structures could be obtained. Mondal et al. previously suggested the interaction between anions (e.g. SO_4^{2-}) and transition-metal ions with unique coordination modes, the

strength of which might change the dynamics of the nuclei and growth rate of the crystals.^[55] Su et al. also found that SO_4^{2-} showed morphology-directing effects on the formation of hexagonal $\text{Co}(\text{OH})_2$ nanoplates.^[35]

It should be mentioned that PEI can improve the solubility of cobalt acetylacetonate through complexing reactions, even though the solubility of cobalt acetylacetonate is 0.48 g per 100 mL H_2O (20 °C). The morphologies and dimensions of hexagonal $\text{Co}(\text{OH})_2$ nanosheets prepared from cobalt acetylacetonate, cobalt nitrate, and cobalt sulfate are summarized in (Table S2). It is found that cobalt acetate is suitable for the synthesis of $\text{Co}(\text{OH})_2$ precursors, owing to the smaller dimensions compared to other cobalt salts. In addition, the effects of the amount of PEI on the $\text{Co}(\text{OH})_2$ dimensions were studied by varying the amount of PEI from 0.5 g (CNS-5P) to 2.0 g (CNS-6P) and 4.0 g (CNS-7P) for the hydrothermal reaction. The morphologies and dimensions of $\text{Co}(\text{OH})_2$ nanosheets are also presented in Figure S6 and Table S2 in the Supporting Information. Clearly, the amount of PEI has a significant influence on the dimensions of $\text{Co}(\text{OH})_2$ precursors, particularly the thickness. When the amount of PEI added to the synthesis is less than 2.0 g, hexagonal nanosheets with similar dimensions can be achieved. A further increase in the amount of PEI, to 4.0 g, leads to a larger side length (ca. 438 nm) and thickness (ca. 156 nm). This could be attributed to the pH increase in the presence of excess PEI, which can accelerate the growth rate of $\text{Co}(\text{OH})_2$. Interestingly, the time-dependent FESEM study of $\text{Co}(\text{OH})_2$ also suggests that hexagonal $\text{Co}(\text{OH})_2$ nanosheets start to form within the first 0.5–2 h (Figure S7). However, the product yield of $\text{Co}(\text{OH})_2$ at 0.5 h is quite low compared with 24 h, as indicated by the pink color of the reaction solution (Figure S8). This can probably be attributed to the slow precipitation reaction between the Co–PEI complex and NaOH. Thus, with the assistance of PEI, hexagonal $\text{Co}(\text{OH})_2$ nanosheets of different dimensions can be controlled by varying the cobalt source, amount of added PEI, and reaction duration.

In comparison, similar to PEI, NH_3 molecules with unshared paired nitrogen atoms can also react with cobalt ions to form a complex, thus controlling the growth rate of $\text{Co}(\text{OH})_2$. However, hexagonal $\text{Co}(\text{OH})_2$ decorated with small nanoparticles that are approximately 50 nm (CNS-8P) in size can be seen in the FESEM images (Figure S9). The difference could be attributed to the much smaller molecules of NH_3 compared to PEI, which are endowed with long-chain polymers. As indicated in Figures 2a and 2b, the clean surface of CNS-1P is caused by steric hindrance of the PEI molecules, avoiding the formation of small nanoparticles on the $\text{Co}(\text{OH})_2$ surface. More importantly, the PEI-mediated hydrothermal synthesis proposed in this study can be successfully extended to fabricate other metal oxides or binary transition-metal oxides, such as MgO, NiO, CoMn_2O_4 , MnCo_2O_4 , and NiCoO_2 . FESEM images of the corresponding hexagonal nanostructured precursors are also given (Figure S10). Previous studies have indicated the promising applications of binary transition-metal oxides as anode materials for lithium-ion batteries.^[56–58] The performances of nanoparticle-decorated Co_3O_4 and binary transition-metal oxides with hexagonal structures will be reported in our future work.

The electrochemical behaviors of ultrathin hexagonal Co_3O_4 nanosheets (CNS-1) were evaluated by using cyclic voltammetry (CV) and galvanostatic charge–discharge cycling. Figure 9a

Figure 9. Electrochemical behaviors of porous hexagonal Co_3O_4 nanosheets: a) CV analysis of the first five cycles at a scan rate of 0.01 mVs^{-1} ; b) typical charge–discharge profiles at a current density of 100 mA g^{-1} .

displays the CV analysis of ultrathin hexagonal Co_3O_4 nanosheets for the first five cycles at a scan rate of 0.01 mVs^{-1} . From the first cycle, the cathodic peaks at 1.22 and 0.92 V could be ascribed to the reduction of Co^{2+} and Co^{3+} to Co^0 , as well as the formation of an irreversible solid-electrolyte interphase (SEI) layer and electrolyte decomposition, respectively.^[15] An anodic peak located at 2.02 V could be attributed to the oxidation of Co^0 to Co^{2+} and Co^{2+} to Co^{3+} , which is in good agreement with previous work.^[24] The possible electrochemical reactions involved are described in previous work.^[59] From the second cycle, the main reduction peak of low intensity is shifted to 1.12 V, probably owing to a polarization effect. It can be seen that the integral area of the second-cycle reduction peak is similar to that of the first cycle. The repeatable anodic peak after the second cycle shows a broad peak at about 2.10 V, consistent with previous studies.^[29]

Figure 9b reveals typical charge and discharge profiles at a current density of 100 mA g^{-1} in the voltage range of 0.005–3.0 V. In the first cycle, porous hexagonal Co_3O_4 nanosheets can deliver specific charge and discharge capacities of 1052 and 1433 mAh g^{-1} , respectively. The increased specific capacity, above the theoretical value (890 mAh g^{-1}), is probably caused by the reversible formation of gel-like polymer films and interfacial lithium storage.^[29] The plateau region of the first discharge curve at around 1.1 V is ascribed to the reduction of Co ions to metallic Co , accompanied by the formation of Li_2O . Previous work confirmed the formation of a polymeric surface layer (SEI) and metallic Co grains in the discharged samples.^[60] The difference in the Co_3O_4 reduction plateau obtained from CV analysis and charge–discharge profiles (Figure 9) can probably be attributed to the different electrochemical test programs. The CV analysis was performed at a relatively low scan rate of 0.01 mV s^{-1} . However, the charge–discharge test was performed over the voltage range of 0.005–3 V at a current density as high as 100 mA g^{-1} , which means the average scan rate in the discharge test was about 0.58 mV s^{-1} , that is, it was much higher than that used for the CV analysis. With the increase in scan rate, the reduction plateau is correspondingly increased, suggesting an increased electrochemical polarization.^[15] It should be noted that the coulombic efficiency of the first cycle was determined to be 73%. For the second cycle, the Co_3O_4 electrode maintained a high reversible capacity of 1004 mAh g^{-1} with a coulombic efficiency of 84%.

The cycling performance of ultrathin hexagonal Co_3O_4 nanosheets (CNS-1) evaluated with a current density of 100 mA g^{-1} is presented in Figure 10a. From the third cycle, the hexagonal Co_3O_4 nanosheets showed high reversibility with a coulombic efficiency of approximately 100%. After 100 cycles, the ultrathin Co_3O_4 nanosheets tested at 100 mA g^{-1} retained a reversible charge capacity of 1007 mAh g^{-1} with a capacity retention of 96%. The morphological stability was investigated through ex situ FESEM analysis of the Co_3O_4 nanosheets (CNS-1) after 100 cycles. Hexagonal and nanosheet structures can clearly be observed in the FESEM images, implying the excellent structure integrity of Co_3O_4 electrode materials (Figure S11). The high performance of CNS-1 achieved in this study is much better than hierarchical network-like Co_3O_4 (ca. 500 mAh g^{-1}

Figure 10. Cycling performances of Co_3O_4 electrode materials: a) ultrathin hexagonal Co_3O_4 nanosheets (CNS-1) and pristine Co_3O_4 (CNS-9) tested at 100 mA g^{-1} ; b) ultrathin hexagonal Co_3O_4 nanosheets (CNS-1) and thick Co_3O_4 nanosheets (CNS-7) tested at 500 mA g^{-1} .

after 30 cycles) and Co_3O_4 nanoflowers (649 mAh g^{-1} after 100 cycles).^[61,62] In contrast, pristine Co_3O_4 (CNS-9) materials synthesized without PEI exhibit poor cycling performance, as indicated by the reversible charge capacity of 555 mAh g^{-1} and capacity retention of 49% after 100 cycles, indicating serious decay in battery performance. In addition, as shown in Figure 10b, when porous Co_3O_4 nanosheets are tested at a high current density of 500 mA g^{-1} (0.56 C ; $1 \text{ C} = 890 \text{ mA g}^{-1}$), good cycling performance (ca. 858 mAh g^{-1}) and high capacity retention (99%) are also observed after 100 cycles. At this high current density, the battery performance of CNS-1 is better than nanorod-assembled Co_3O_4 hexapods.^[63]

Interestingly, as illustrated in Figure 10b, when thick Co_3O_4 nanosheets (CNS-7), derived from hexagonal $\text{Co}(\text{OH})_2$ nanosheets with a thickness of approximately 156 nm , are tested at the same current density, good cycling performance and high capacity retention (98%) are also confirmed. However, after 100 cycles, the specific charge capacity of the thick Co_3O_4 nanosheets (ca. 731 mAh g^{-1}) is lower than that of the ultrathin nanosheets (ca. 1007 mAh g^{-1}). It should be noted that slightly unstable specific capacities of Co_3O_4 were found during the cycling performance test, in comparison with previous studies.^[13,14] Apart from the temperature effect, this phenomenon might be associated with variations in the electron-transport network caused by the severe volume change of Co_3O_4 during repeated charge–discharge cycles. Electron transport in nano-

structured semiconducting materials followed a random walk in the electrochemical process.^[29] Therefore, electron transport in this study might be significantly affected by the contact points between Co_3O_4 and carbon additives/current collectors, which, in turn, shows significant effects on the lithium-storage capacity. To enhance electron transport, it is recommended that the as-prepared Co_3O_4 electrode disc should be pressed before testing.

The rate capability of electrode materials is an important parameter for battery applications.^[64] As shown in Figure 11, the

Figure 11. Rate capabilities of hexagonal Co_3O_4 nanosheets at various current densities.

specific charge capacities of ultrathin Co_3O_4 nanosheets (CNS-1) tested at 100, 200, 500, 1000, and 2000 mA g^{-1} are about 1037, 897, 809, 467, and 418 mAh g^{-1} , respectively. When the current density returns to 100 mA g^{-1} , a high charge capacity of 1019 mAh g^{-1} can be still achieved. During the charge–discharge process, the coulombic efficiency is well maintained at approximately 100%. It is also found that ultrathin hexagonal Co_3O_4 nanosheets exhibit superior rate capability in comparison with state-of-the-art Co_3O_4 -based anode materials, such as graphene-encapsulated mesoporous Co_3O_4 (ca. 264 mAh g^{-1} at 2000 mA g^{-1}).^[65] Previous work has also reported that macroporous Co_3O_4 platelets exhibit excellent high rate capabilities, as compared to Co_3O_4 nanoparticles and rod-like nanoclusters.^[66]

In this work, porous hexagonal Co_3O_4 nanosheets demonstrate superior battery performance, including high specific capacity, good capacity retention, and excellent rate capability. On one hand, the exposed (111) crystal facets with ultrathin structures provide reactive sites for reaction with lithium ions, which can facilitate the diffusion of lithium ions by providing them with a short diffusion length during charge–discharge processes. Previous work suggested that high-energy surfaces show a large density of low-coordinated atoms situated on steps and kinks, with high reactivity.^[67] A high density of cobalt ions on (111) facets of Co_3O_4 can result in the high utilization of electrode materials. The high catalytic activities of Co_3O_4 with exposed (111) facets, in comparison with conventionally prepared Co_3O_4 , have also been reported in previous studies,

such as methanol decomposition and methane conversion.^[68,69] On the other hand, the multiscale porous structure of hexagonal Co_3O_4 is advantageous for improving the lithium-storage capacity and cycle life. For example, 1) it can effectively alleviate the problem of pulverization of the electrode material caused by volume expansion during repeated charge–discharge cycles; 2) it can significantly enhance the diffusion of Li-containing electrolytes to active sites for electrochemical reactions, thus reducing the lithium-ion diffusion length; 3) it can also contribute towards additional lithium storage capacity, owing to the interfacial storage mechanism.^[13,29] In summary, a general strategy has been successfully developed for ultrathin hexagonal Co_3O_4 nanosheets, based on a PEI-mediated hydrothermal route. The improved electrochemical performance is attributed to the synergistic effects of the reactive facets and the ultrathin and porous features of hexagonal Co_3O_4 nanosheets.

3. Conclusions

A general PEI-mediated synthesis route is successfully developed for ultrathin hexagonal Co_3O_4 nanosheets with a high percentage of (111) reactive facets and multiscale pores. It is found that PEI plays multiple crucial roles in the formation of hexagonal nanosheets. The unique Co_3O_4 nanostructures demonstrate a high specific capacity, excellent cyclability, and high rate capability when tested as anode materials for lithium-ion batteries. The results also suggest that the improved performance may be attributed to the combined effects of the high percentage of reactive facets as well as the ultrathin and porous features of the hexagonal Co_3O_4 nanosheets. More importantly, the PEI-mediated synthesis strategy has great potential to be applied to fabricate other transition-metal oxides. Thus, the proposed synthesis strategy in this study can open up new avenues in the development of next-generation anode materials (e.g. binary transition-metal oxides) endowed with reactive facets as well as ultrathin and porous structures for high-performance lithium-ion batteries.

Experimental Section

Synthesis of $\text{Co}(\text{OH})_2$ Precursors and Co_3O_4 Products

In a typical synthesis, cobalt acetate tetrahydrate (1.25 g) ($\geq 98.0\%$, Sigma-Aldrich) and branched PEI (1.0 g) (99.0%, Sigma-Aldrich) were dissolved in deionized water (30 mL) (Millipore, Inc., 18 $\text{M}\Omega\text{ cm}^{-1}$) at room temperature, followed by adding 0.33 M sodium hydroxide (30 mL) ($\geq 98.0\%$, Sigma-Aldrich). After stirring for 30 min at room temperature, the above-mentioned mixed solution was immediately transferred into a 100 mL Teflon-lined stainless-steel autoclave and placed in an electric oven with air circulating at 120 °C for 12 h. After hydrothermal treatment, the reddish precursors were harvested by vacuum filtration and washed with sufficient deionized water and ethanol three times. After that, the as-prepared precursors were dried in a vacuum oven at 60 °C for 24 h. To prepare Co_3O_4 , heat treatment of the dried precursors was performed in an air atmosphere at 400 °C for 2 h with a ramping rate of 2.5 °C min^{-1} . The as-prepared Co_3O_4 precursors and products, denoted as CNS-1P and CNS-1, respectively, were directly

used for material characterization and battery performance evaluations. For comparison, Co(OH)_2 precursors were also fabricated with various cobalt salts (e.g. CNS-2P: cobalt acetylacetonate; CNS-3P: cobalt nitrate; CNS-4P: cobalt sulfate). In addition, the effect of the amount of PEI (e.g. CNS-5P: 0.5 g PEI; CNS-6P: 2.0 g PEI; CNS-7P: 4.0 g PEI) on the precursor morphologies and dimensions were also systemically investigated in this study. To further understand the roles of PEI, an ammonium solution (35 wt%, Acros Organics), instead of PEI, was used as a structure-directing agent for the precursor synthesis (CNS-8P). Also, a pristine Co_3O_4 sample (CNS-9P) was also prepared with the same procedures in the absence of PEI as a reference sample. All as-prepared Co_3O_4 samples were obtained by heat treatment of Co(OH)_2 precursors at 400°C for 2 h in air. The syntheses details for the Co(OH)_2 precursors and Co_3O_4 products are listed in Table S1.

Material Characterization

Morphology and structure analyses of Co(OH)_2 precursors and Co_3O_4 products were performed on a field emission scanning electron microscope (Hitachi S4800) and a transmission electron microscope (FEI Tecnai G2 20 scanning) equipped with SAED. Crystal-phase structures of Co(OH)_2 and Co_3O_4 were also identified by using an X-ray diffractometer (Bruker) equipped with $\text{CuK}_{\alpha 12}$ X-ray radiation and a LynxEye detector. The scanning range of 2θ was $10\text{--}80^\circ$ with a step size of 0.02° and a scan speed of 0.2° s^{-1} per step. DTG analyses of the Co(OH)_2 precursors and Co_3O_4 products were carried out on an EXSTAR TG/DTA 6300 instrument (SII Nano-technology, Tokyo, Japan) under an air flow from room temperature to 800°C with a heating rate of $10^\circ\text{C min}^{-1}$. FTIR spectra were recorded on a Shimadzu spectrometer in the range of $500\text{--}4000\text{ cm}^{-1}$ with a resolution of 4 cm^{-1} . The oxidation states of elements in Co(OH)_2 and Co_3O_4 were measured on an X-ray photoelectron spectrometer (Model PHI5600). The BE values were referenced to the C 1s peak at 284.6 eV . The specific surface area and pore-size distribution of Co(OH)_2 precursors and Co_3O_4 products were recorded on Micrometrics ASAP 2020, using N_2 adsorption-desorption isotherm at liquid-nitrogen temperature (-196°C). BET and BJH methods were applied to calculate the specific surface area and pore-size distribution, respectively. The as-prepared precursors and products used during material characterization were CNS-1P and CNS-1, unless otherwise specified.

Electrochemical Measurements

The electrochemical performances of ultrathin hexagonal Co_3O_4 nanosheets (CNS-1), thick Co_3O_4 nanosheets (CNS-7), and pristine Co_3O_4 (CNS-9) were tested on a battery-testing system (LAND CT2001A, Wuhan Jinnuo Electronics, Ltd., China) at various current densities (e.g. 100 and 500 mA g^{-1}), using standard 2025-type coin cells with a cutoff voltage range from 0.005 to 3.0 V versus Li^+/Li . The working electrodes consisted of $70\text{ wt}\%$ active materials (Co_3O_4), $15\text{ wt}\%$ conductivity agents (acetylene black, Super P), and $15\text{ wt}\%$ binders (polyvinylidene fluoride, PVDF) in *N*-methyl-2-pyrrolidinone (NMP) solvent. The as-prepared Co_3O_4 slurry was uniformly coated onto copper foil by using an automatic film applicator (AFA-II, Shanghai Pushen Chemical Machinery Co. Ltd., China) and dried in a vacuum oven at 120°C for 12 h. The loading of anode materials was $1.5 \pm 0.1\text{ mg cm}^{-2}$. The Co_3O_4 anode disc (diameter: 18 mm) was fabricated by cutting coated Cu foil with a compact and precision disc cutter (MSK-T-10, MTI Corporation). Lithium foil (thickness: 1.8 mm) was used as the counter/reference electrode. The Co_3O_4 working electrode was separated from the

lithium counter electrode by using a polypropylene microporous membrane (Celgard 2400, thickness: $25\text{ }\mu\text{m}$). For the electrolyte, 1 mol L^{-1} LiPF_6 dissolved in a mixture of $50\text{ vol}\%$ ethylene carbonate (EC) and $50\text{ vol}\%$ diethyl carbonate (DEC) was employed. Coin cells were assembled in an argon-filled glove-box (MB-10, MBRAUN) with $<0.5\text{ ppm}$ of oxygen and water, using a compact hydraulic crimping machine (MSK-110, MTI Corporation). CV curves were recorded on a BioLogic electrochemical station (DHS Instruments Co., Ltd.) in the potential window of $0.005\text{--}3.0\text{ V}$ (vs. Li/Li^+) at a scanning rate of 0.01 mV s^{-1} at room temperature.

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- [1] A. S. Aricò, P. Bruce, B. Scrosati, J.-M. Tarascon, W. van Schalkwijk, *Nat. Mater.* **2005**, *4*, 366–377.
- [2] H.-G. Jung, M. W. Jang, J. Hassoun, Y.-K. Sun, B. Scrosati, *Nat. Commun.* **2011**, *2*, 516.
- [3] Z. Bai, N. Fan, C. Sun, Z. Ju, C. Guo, J. Yang, Y. Qian, *Nanoscale* **2013**, *5*, 2442–2447.
- [4] S. M. Abbas, S. T. Hussain, S. Ali, N. Ahmad, N. Ali, K. S. Munawar, *Electrochim. Acta* **2013**, *105*, 481–488.
- [5] J. M. Tarascon, M. Armand, *Nature* **2001**, *414*, 359–367.
- [6] L. Li, K. H. Seng, Z. Chen, Z. Guo, H. K. Liu, *Nanoscale* **2013**, *5*, 1922–1928.
- [7] T. Bhardwaj, A. Antic, B. Pavan, V. Barone, B. D. Fahlman, *J. Am. Chem. Soc.* **2010**, *132*, 12556–12558.
- [8] S. H. Choi, Y. C. Kang, *Small* **2014**, *10*, 474–478.
- [9] D. Y. W. Yu, H. E. Hoster, S. K. Batabyal, *Sci. Rep.* **2014**, *4*, 4562.
- [10] J. Ye, W. Liu, J. Cai, S. Chen, X. Zhao, H. Zhou, L. Qi, *J. Am. Chem. Soc.* **2010**, *133*, 933–940.
- [11] H. Wang, D. Ma, X. Huang, Y. Huang, X. Zhang, *Sci. Rep.* **2012**, *2*, 701.
- [12] P. Poizot, S. Laruelle, S. Grugeon, L. Dupont, J. M. Tarascon, *Nature* **2000**, *407*, 496–499.
- [13] J. Guo, L. Chen, X. Zhang, B. Jiang, L. Ma, *Electrochim. Acta* **2014**, *129*, 410–415.
- [14] J. Guo, B. Jiang, X. Zhang, L. Tang, Y.-h. Wen, *J. Mater. Chem. A* **2015**, *3*, 2251–2257.
- [15] L. Jin, X. Li, H. Ming, H. Wang, Z. Jia, Y. Fu, J. Adkins, Q. Zhou, J. Zheng, *RSC Adv.* **2014**, *4*, 6083–6089.
- [16] J. Wang, N. Yang, H. Tang, Z. Dong, Q. Jin, M. Yang, D. Kisailus, H. Zhao, Z. Tang, D. Wang, *Angew. Chem. Int. Ed.* **2013**, *52*, 6417–6420; *Angew. Chem.* **2013**, *125*, 6545–6548.
- [17] Y. Li, B. Tan, Y. Wu, *Nano Lett.* **2008**, *8*, 265–270.
- [18] X. Zhang, Y. Zhao, C. Xu, *Nanoscale* **2014**, *6*, 3638–3646.
- [19] X. W. Lou, D. Deng, J. Y. Lee, J. Feng, L. A. Archer, *Adv. Mater.* **2008**, *20*, 258–262.
- [20] T. He, D. Chen, X. Jiao, Y. Wang, *Adv. Mater.* **2006**, *18*, 1078–1082.
- [21] Y. Wang, H. J. Zhang, J. Wei, C. C. Wong, J. Lin, A. Borgna, *Energy Environ. Sci.* **2011**, *4*, 1845–1854.
- [22] X. Qing, S. Liu, K. Huang, K. Lv, Y. Yang, Z. Lu, D. Fang, X. Liang, *Electrochim. Acta* **2011**, *56*, 4985–4991.
- [23] X.-Y. Xue, S. Yuan, L.-L. Xing, Z.-H. Chen, B. He, Y.-J. Chen, *Chem. Commun.* **2011**, *47*, 4718–4720.
- [24] L. Hu, N. Yan, Q. Chen, P. Zhang, H. Zhong, X. Zheng, Y. Li, X. Hu, *Chem. Eur. J.* **2012**, *18*, 8971–8977.

- [25] D. Liu, X. Wang, X. Wang, W. Tian, Y. Bando, D. Golberg, *Sci. Rep.* **2013**, *3*, 2543.
- [26] N. Yan, L. Hu, Y. Li, Y. Wang, H. Zhong, X. Hu, X. Kong, Q. Chen, *J. Phys. Chem. C* **2012**, *116*, 7227–7235.
- [27] F. Zhan, B. Geng, Y. Guo, *Chem. Eur. J.* **2009**, *15*, 6169–6174.
- [28] M. Y. Son, J. H. Kim, Y. C. Kang, *Electrochim. Acta* **2014**, *116*, 44–50.
- [29] B. Wang, X.-Y. Lu, Y. Tang, *J. Mater. Chem. A* **2015**, *3*, 9689–9699.
- [30] X. Xiao, X. Liu, H. Zhao, D. Chen, F. Liu, J. Xiang, Z. Hu, Y. Li, *Adv. Mater.* **2012**, *24*, 5762–5766.
- [31] G.-L. Xu, J.-T. Li, L. Huang, W. Lin, S.-G. Sun, *Nano Energy* **2013**, *2*, 394–402.
- [32] Y. Hou, H. Kondoh, M. Shimojo, T. Kogure, T. Ohta, *J. Phys. Chem. B* **2005**, *109*, 19094–19098.
- [33] S. Xiong, C. Yuan, X. Zhang, B. Xi, Y. Qian, *Chem. Eur. J.* **2009**, *15*, 5320–5326.
- [34] P. Zhan, *J. Alloys Compd.* **2009**, *478*, 823–826.
- [35] D. Su, X. Xie, P. Munroe, S. Dou, G. Wang, *Sci. Rep.* **2014**, 6519.
- [36] Y. Tang, Y. Zhang, J. Deng, J. Wei, H. L. Tam, B. K. Chandran, Z. Dong, Z. Chen, X. Chen, *Adv. Mater.* **2014**, *26*, 6111–6118.
- [37] Y. Yin, R. M. Rioux, C. K. Erdonmez, S. Hughes, G. A. Somorjai, A. P. Alivisatos, *Science* **2004**, *304*, 711–714.
- [38] P. Su, S. Liao, F. Rong, F. Wang, J. Chen, C. Li, Q. Yang, *J. Mater. Chem. A* **2014**, *2*, 17408–17414.
- [39] D. Su, S. Dou, G. Wang, *Nano Res.* **2014**, *7*, 794–803.
- [40] J. Zhu, L. Bai, Y. Sun, X. Zhang, Q. Li, B. Cao, W. Yan, Y. Xie, *Nanoscale* **2013**, *5*, 5241–5246.
- [41] T. Zhu, J. S. Chen, X. W. Lou, *J. Mater. Chem.* **2010**, *20*, 7015–7020.
- [42] S. W. Hwang, A. Umar, S. H. Kim, S. A. Al-Sayari, M. Abaker, A. Al-Hajry, A. M. Stephan, *Electrochim. Acta* **2011**, *56*, 8534–8538.
- [43] X.-H. Xia, J.-P. Tu, Y.-J. Mai, X.-L. Wang, C.-D. Gu, X.-B. Zhao, *J. Mater. Chem.* **2011**, *21*, 9319–9325.
- [44] H. Cai, X. An, J. Cui, J. Li, S. Wen, K. Li, M. Shen, L. Zheng, G. Zhang, X. Shi, *ACS Appl. Mater. Interfaces* **2013**, *5*, 1722–1731.
- [45] W.-T. Kuo, H.-Y. Huang, M.-J. Chou, M.-C. Wu, Y.-Y. Huang, *J. Nanomater.* **2011**, *2011*, 646538.
- [46] C. Liang, D. Cheng, S. Ding, P. Zhao, M. Zhao, X. Song, F. Wang, *J. Power Sources* **2014**, *251*, 351–356.
- [47] Y. Xiao, C. Hu, M. Cao, *J. Power Sources* **2014**, *247*, 49–56.
- [48] K. Deori, S. K. Ujjain, R. K. Sharma, S. Deka, *ACS Appl. Mater. Interfaces* **2013**, *5*, 10665–10672.
- [49] H.-W. Shim, Y.-H. Jin, S.-D. Seo, S.-H. Lee, D.-W. Kim, *ACS Nano* **2011**, *5*, 443–449.
- [50] V. N. Kislenko, L. P. Oliynyk, *J. Polym. Sci. Part A* **2002**, *40*, 914–922.
- [51] R. V. Benjaminsen, M. A. Matthebjerg, J. R. Henriksen, S. M. Moghimi, T. L. Andresen, *Mol. Ther.* **2013**, *21*, 149–157.
- [52] A. Chatterjee, A. Priyam, S. C. Bhattacharya, A. Saha, *Colloids Surf. A* **2007**, *297*, 258–266.
- [53] H. Liang, J. M. Raitano, L. Zhang, S.-W. Chan, *Chem. Commun.* **2009**, 48, 7569–7571.
- [54] C. Li, X. Yin, L. Chen, Q. Li, T. Wang, *Chem. Eur. J.* **2010**, *16*, 5215–5221.
- [55] A. K. Mondal, D. Su, S. Chen, A. Ung, H.-S. Kim, G. Wang, *Chem. Eur. J.* **2015**, *21*, 1526–1532.
- [56] J. Li, S. Xiong, X. Li, Y. Qian, *Nanoscale* **2013**, *5*, 2045–2054.
- [57] L. Li, Y. Q. Zhang, X. Y. Liu, S. J. Shi, X. Y. Zhao, H. Zhang, X. Ge, G. F. Cai, C. D. Gu, X. L. Wang, J. P. Tu, *Electrochim. Acta* **2014**, *116*, 467–474.
- [58] J. Li, J. Wang, X. Liang, Z. Zhang, H. Liu, Y. Qian, S. Xiong, *ACS Appl. Mater. Interfaces* **2014**, *6*, 24–30.
- [59] M. V. Reddy, Z. Beichen, L. J. e. Nicholette, Z. Kaimeng, B. V. R. Chowdari, *Electrochem. Solid-State Lett.* **2011**, *14*, A79–A82.
- [60] X. Wang, X. L. Wu, Y. G. Guo, Y. Zhong, X. Cao, Y. Ma, J. Yao, *Adv. Funct. Mater.* **2010**, *20*, 1680–1686.
- [61] X. X. Zhang, Q. S. Xie, G. H. Yue, Y. Zhang, X. Q. Zhang, A. L. Lu, D. L. Peng, *Electrochim. Acta* **2013**, *111*, 746–754.
- [62] J. S. Chen, T. Zhu, Q. H. Hu, J. Gao, F. Su, S. Z. Qiao, X. W. Lou, *ACS Appl. Mater. Interfaces* **2010**, *2*, 3628–3635.
- [63] L. Wang, B. Liu, S. Ran, H. Huang, X. Wang, B. Liang, D. Chen, G. Shen, *J. Mater. Chem.* **2012**, *22*, 23541–23546.
- [64] H. Sun, M. Ahmad, J. Zhu, *Electrochim. Acta* **2013**, *89*, 199–205.
- [65] X. Yang, K. Fan, Y. Zhu, J. Shen, X. Jiang, P. Zhao, C. Li, *J. Mater. Chem.* **2012**, *22*, 17278–17283.
- [66] Y. Lu, Y. Wang, Y. Zou, Z. Jiao, B. Zhao, Y. He, M. Wu, *Electrochem. Commun.* **2010**, *12*, 101–105.
- [67] D. Su, M. Ford, G. Wang, *Sci. Rep.* **2012**, *2*, 924.
- [68] L. Chen, J. Hu, R. Richards, S. Prihodko, S. Kodambaka, *Nanoscale* **2010**, *2*, 1657–1660.
- [69] L. Hu, Q. Peng, Y. Li, *J. Am. Chem. Soc.* **2008**, *130*, 16136–16137.

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