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Real-time observation of phase transition from layered to spinel phase under electron beam irradiation

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Abstract

Transition metal hydroxides (TM(OH)₂) have drawn significant attention for their potential applications in the environmental and energy field. In this study, we investigated the phase transition of cobalt hydroxide (Co(OH)₂) under electron beam irradiation using in situ high-resolution transmission electron microscopy. Both the α - and β -Co(OH)₂ phases underwent a phase transition to a spinel Co_3O_4 phase, forming nanograins with a porous morphology. However, the α -Co(OH)₂ showed a faster phase transition and dramatic volume shrinkage during the phase transition. Our results provide a detailed explanation of the mechanism behind the deterioration of the layered structure and the emergence of defects during the phase transition.

Keywords Co(OH)₂, Spinel Co₃O₄, Phase transition, Electron beam irradiation

Introduction

Transition metal hydroxides (TM(OH)₂) have been extensively studied for various applications in the environmental and energy fields, including for water splitting, catalysts, supercapacitors and batteries (Jia et al. 2017; Kim et al. 2018; Ma et al. 2016; Ye et al. 2018). Recently, thanks to the great interest in lithium-ion batteries, TM(OH)₂, used as precursors in cathode active materials, has attracted wide attention (Amou et al. 2021; Park et al. 2018; Qian et al. 2020) . Among the various types of $TM(OH)_2$, cobalt hydroxides (Co(OH)₂)

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have two distinctive phases: α - and β -Co(OH)₂ phase (Jayashree and Kamath 1999; Liu et al. 2005; Ma et al. 2006). β -Co(OH)₂ adopts the structure of the mineral brucite, in which the hexagonal packing of hydroxyl ions coordinated with divalent Co(II) cations occupies alternate rows of octahedral sites. On the other hand, α -Co(OH)₂ is an isomorph-layered double hydroxide with a hydrotalcite-like structure consisting of positively charged brucite-like layers and negatively charged anions in the hydrated interlayer regions. The hydrotalcite-like structure is generally represented as $[M_{1-x}^{II}M_{x}^{III}(OH)_{2}]^{x+}(A^{n-})_{x/n} \cdot mH_{2}O$ where M_{1-x}^{II} are divalent cations, M_x^{III} are trivalent cations, A^{n-} are interlayer anions with negative charge *n*, and *m* is the number of water molecules in the interlayer region. Since the anions and water molecules are intercalated in the interlayer region, α -Co(OH)₂ has a larger interlayer spacing (7–8 Å) than β -Co(OH)₂ (4.6 Å) (Liu et al. 2005).

Electron irradiation offers the most basic form of in situ experiment in the transmission electron microscope (TEM) system. The accelerated electrons (typically 200-300 kV) trigger structural changes in local areas, which can be continuously monitored in real time. The electron



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irradiation typically causes crystallization/amorphization or phase changes from one crystalline phase to another, depending on the experimental conditions and the materials (Ishimaru et al. 2003; Jiang et al. 2019; Parajuli et al. 2020; Yao et al. 2014). These electron beam effects have typically been treated as electron beam damage, to be mostly avoided; however, sometimes the artificial phase transitions induced by electron beam have been studied to better understand the complex mechanism of the phase change in a real environment.

For example, Jing et al. observed direct crystallization and amorphization in GeSb₂Te₄ thin films under electron beam irradiation, where the melting process was absent. The authors claimed that the nonthermal amorphization contributed to the knock-on collision effect of the electron beam (Jiang et al. 2019). In addition, the phase transition induced by the electron beam irradiation provided crucial information about the structural changes in the actual electrochemical reactions. Parajuli et al. investigated the electron beam-induced spinel to defective rock-salt phase transition in MgCrMnO₄ and found that the emergence of oxygen vacancies reduced the difference in free energy of the two phases, overcoming the kinetic barrier and facilitating cation migration, which eventually led to a defective rock-salt phase transition (Parajuli et al. 2020).

While the α - and β -Co(OH)₂ are not typically used as electrode materials in lithium-ion batteries, they have a similar layered structure to materials that are commonly used as cathodes, such as LiCoO₂ and LiNi_{1-x-y}Co_xMn_yO₂ (NCM). The phase changes and defect formations that occur in the reaction or degradation process of these cathode materials can also be observed in Co(OH)₂. In this study, we directly observed the phase transition from a layered structure to a spinel structure in Co(OH)₂ under electron beam irradiation. Both the α - and β -Co(OH)₂ transformed into nanograin spinel Co₃O₄ during the electron beam irradiation. The transition from the layered phase to the spinel phase was accompanied by enormous structural changes, including significant volume shrinkage and many defects.

Experimental methods

Synthesis of α -Co(OH)₂ and β -Co(OH)₂ particles

The α -Co(OH)₂ and β -Co(OH)₂ particles were synthesized under ambient conditions according to a previous work (Park et al. 2022b). For α -Co(OH)₂, cobalt chloride hexahydrate (10 mM, CoCl₂·6H₂O, Sigma-Aldrich), sodium chloride (50 mM, NaCl, Oriental Chemical Industry), hexamethylenetetramine (60 mM, C₆H₁₂N₄, 99.0%, Sigma-Aldrich) were dissolved in 150 mL of a 1:9 mixture of ethanol and deionized water. The solution was heated in an oil bath at 90 °C for one hour, resulting in a suspension with green particles. Then, the suspended product was centrifuged at 3500 rpm for 15 min and washed several times with deionized water and anhydrous ethanol. The final green particles were fully dried at room temperature. The synthesis procedure of β -Co(OH)₂ was the same as that of α -Co(OH)₂; however, NaCl was not included in the initial solution. For β -Co(OH)₂, pink powders were obtained.

Electron microscopy

Scanning electron microscope (SEM) images were taken using a ZEISS SIGMA 300 VP. The morphology of α and β -Co(OH)₂ particles was studied through scanning electron microscopy (SEM). Transmission electron microscopy (TEM) experiments were performed on a FEI Tecnai F30 operated at the accelerated voltage of 300 kV. The dose rate for the electron beam irradiation was $2 \times 10^4 \text{ e}^-/\text{Å}^2 \cdot \text{s}$, and the sample drift during the irradiation was corrected by manual operation. The Co(OH)₂ powders were well dispersed in ethanol and dropped onto a lacey carbon grid for the TEM observation. The cross-sectional TEM specimens were prepared by focused ion beam (FIB), following the typical TEM specimen preparation method for 2D materials using a Quanta 3D FEG (Vilá et al. 2016; Yang et al. 2019). A carbon and Pt layer were deposited to protect the $Co(OH)_2$ sample during the FIB sampling and milling process. The damage caused by the Ga ion beam of 30 kV was removed with a low voltage of 5 kV.

Results and discussion

Figure 1a, b shows the SEM images of $\alpha\text{-Co(OH)}_2$ and β -Co(OH)₂, respectively. In the α -Co(OH)₂ sample, two shapes can be observed, hexagonal microplates and the flower-shaped α -Co(OH)₂. The hexagonal microplate contains a typical 2D structure, while the flower-shaped sample is formed by the aggregation of several hexagonal microplates, resulting in a 3D structure. The lateral size of the α -Co(OH)₂ varies from 1 to 6 μ m, depending on the shapes; the flower-shaped α -Co(OH)₂ tends to have a smaller size compared to the hexagonal microplates (Li et al. 2021). However, both the microplates and flower-shaped structure have the same crystal structure of α -Co(OH)₂ as observed by X-ray diffraction in Fig. 1c. On the other hand, β -Co(OH)₂ has a rather uniform shape and size. The β -Co(OH)₂ sample shows hexagonal microplates, and the average lateral size is 6 µm. The X-ray diffraction (XRD) patterns in Fig. 1c show that the XRD results of α -Co(OH)₂ and β -Co(OH)₂ agree well with the previous reported data, and both phases were synthesized with high quality without any other phases (Liu et al. 2005). The interlayer spacings for α -Co(OH)₂ have been reported to vary depending on the different



Fig. 1 SEM images of a α -Co(OH)₂ and b β -Co(OH)₂ microplates, c XRD patterns of α - and β -Co(OH)₂. d Schematic of atomic structure of α -Co(OH)₂ and β -Co(OH)₂.

types of intercalated anions and their concentrations (Hu et al. 2009; Ismail et al. 1995; Rajamathi et al. 2000; Tian et al. 2011). The interlayer spacing in our α -Co(OH)₂ was determined in the XRD to be as 8.03 Å. The schematics of the atomic structures of α - and β -Co(OH)₂ are displayed in Fig. 1d.

Figures 2 and 3 show a time series of high-resolution TEM images and the corresponding fast Fourier transform (FFT) patterns of α -Co(OH)₂ and β -Co(OH)₂ under electron beam irradiation, respectively. The TEM data were captured continuously, and specific data were then selected. The high-resolution images show some changes in contrast over time. The differences are more clearly observed in FFT patterns, as shown in Fig. 2a2–d2 and Fig. 3a2–d2. Initially, the FFT pattern shows the typical diffractograms of α -Co(OH)₂ and β -Co(OH)₂ observed from the [001] zone axis, respectively. However, in the case of α -Co(OH)₂, there are some hazy intensities near the diffraction peaks, forming elongated peaks along the outer direction as shown in Fig. 2a2 ({110} peaks

indicated by the cyan arrow). These extended signals indicate that some regions where the electron beam was irradiated already transformed into cobalt oxyhydroxide (CoOOH) phase during the first image acquisition time $(\sim 0.13 \text{ s})$. It is worth noting that CoOOH contains the same octahedral cobalt framework as Co(OH)₂ but with a slightly smaller lattice parameter a. Consequently, the peaks of CoOOH appear near those of Co(OH)₂, but in the outer region of the diffraction space (Deliens and Goethals 1973). Hydrogen atoms can be easily kicked out by electron beam irradiation, resulting in a rapid phase transition into CoOOH. In contrast, β -Co(OH)₂ in Fig. 3a2 shows sharp peaks at the first image acquisition time, suggesting that β -Co(OH)₂ is more resistant to electron beam irradiation compared to α -Co(OH)₂. After some electron beam irradiation, both α -Co(OH)₂ and β -Co(OH)₂ show a CoOOH phase transition, as shown in Figs. 2b2 and 3b2.

After 30 s of electron beam irradiation, both the α -Co(OH)₂ and β -Co(OH)₂ show drastic changes. The



Fig. 2 Time series of high-resolution TEM images (a1–d1) and corresponding fast Fourier transform patterns (a2–d2) of α -Co(OH)₂ during the e-beam irradiation. The data were selected for 0 s, 30 s, 120 s and 300 s. Scale bar is 10 nm. FFT data are rotated and magnified for a clear observation



Fig. 3 Time series of high-resolution TEM images (a1–d1) and corresponding fast Fourier transform patterns (a2–d2) of β -Co(OH)₂ during the electron beam irradiation. The data were selected for 0 s, 30 s, 120 s and 300 s. Scale bar is 10 nm. FFT data are rotated and magnified for a clear observation

structural changes could be clearly observed in the FFT patterns: New peaks from the spinel Co_3O_4 phase emerge, forming a new hexagon pattern which is rotated

by 30° from the initial {100} peaks of the Co(OH)₂ (Figs. 2b2 and 3b2). Although both the α -Co(OH)₂ and β -Co(OH)₂ show the same phase transition to the

spinel Co₃O₄, the detailed phase evolution is different. In α -Co(OH)₂, the newly emerged spinel Co₃O₄ peaks appear strong after 30 s of electron beam irradiation, as displayed in Fig. 2b2. However, in β -Co(OH)₂, the same spinel Co₃O₄ peaks emerge with relatively weak intensity, as shown in Fig. 3b2, suggesting the fact that the phase transition from Co(OH)₂ to spinel occurred faster in α -Co(OH)₂ than in β -Co(OH)₂. Indeed, the electron beam interacted more sensitively with α -Co(OH)₂, causing a rapid decrease in its crystallinity and inducing a faster phase transition upon exposure to the electron beam. Further electron beam irradiation resulted in the diminishing of Co(OH)₂ and CoOOH phases; eventually, the spinel Co₃O₄ phase dominated most of the irradiated area in both α -Co(OH)₂ than in β -Co(OH)₂, as shown in Figs. 2c2 and 3c2. However, some CoOOH peaks remained after 300 s of irradiation, as shown in Figs. 2d2 and 3d2 (indicated by cyan arrow).

To examine the phase transition of $Co(OH)_2$ in more detail, cross-sectional samples are investigated. Figure 4 displays cross-sectional HR-TEM images of the $Co(OH)_2$ under electron beam irradiation. As the electron beam irradiated the sample, the layered structure began to show some local degradation, in which the atomic structure appeared to deviate from the typical layered structure, showing some disordered phases, as in Fig. 4b. The disordered regions were approximately a few nanometers in

size. In addition, the layers broke into smaller grains and some of the layers were tilted or bent depending on the location. Further electron beam irradiation resulted in roughening of the surface and the overall surface moved downward. The total thickness of α -Co(OH)₂ shrank significantly after the electron beam irradiation (Additional file 1), which might be due to the evaporation of water molecules between the layers. The electron beam irradiation eventually led to the formation of spinel phases, as displayed in Fig. 4e, f. The d-spacing values are consistent with the spinel Co_3O_4 phase. The spinel phase exhibited a polycrystalline FFT comprising of nanograins, in contrast to the single-crystalline appearance observed in the top view FFT (Figs. 2 and 3). The inconsistency between the results from the cross section and the plane-view sample could be attributed to the tilting of the nano-sized grains of spinel during the electron beam irradiation. Distinguishing the tilted nanograins in a specific direction only from the top-view diffraction pattern is difficult, as the tilted diffraction overlaps with other patterns. For example, if the spinel nanograins were tilted with respect to the [112]_{spinel} (zone axis for cross-sectional sample), the rotation of nanograins would not be observable from the [111]_{spinel} since the FFT pattern of the tilted nanograins overlapped those of the original spinel phase. Thus the FFT pattern for the [111]_{spinel} zone axis showed a single-crystalline feature in spite of the rotation



Fig. 4 High resolution of cross-sectional TEM images of α -Co(OH)₂ after electron beam irradiation for **a** 0 s, **b** 15 s, **c** 30 s, **d** 60 s and **e** 80 s. **f** Total FFT pattern of cross section of α -Co(OH)₂. Scale bar is 5 nm

of the nanograins (see Additional file 1 for details). The size of the nanograins is expected to be ~5 nm based on the length of the discontinuity observed in Fig. 4c. It appears that an orientational relationship exists between $Co(OH)_2$ and spinel Co_3O_4 in the FFT pattern observed from the top view, such as $[001]_{Co(OH)2}$ || $[111]_{Co3O4}$ and $(110)_{Co(OH)2}$ || $(\bar{1}10)_{Co3O4}$. However, as the spinel Co_3O_4 nanograins form during the phase transition, the tilting of these nanograins becomes evident when observed in the cross-sectional view. Consequently, the previously observed orientational relationship in the top view is no longer valid.

After a long time of electron beam irradiation during which the phase change no longer occurred, the final structure was further investigated. Figure 5 shows the high-resolution TEM and high-angle annular dark field-scanning transmission electron microscopy (HAADF-STEM) image of α -Co(OH)₂ after electron beam irradiation. Both TEM and HAADF-STEM images showed contrast variation with granular features, indicating that the converted spinel Co_3O_4 contained a porous morphology. The size of the contrast variation varied but was comparable to the size of nanograins shown in Fig. 4c. It is worth noting that β -Co(OH)₂ also showed similar contrast variation, indicating that the morphological change did not involve the extraction of water molecules. The porous morphology is a common feature shared by both α -Co(OH)₂ and β -Co(OH)₂.

The phase changes that occur when $Co(OH)_2$ is exposed to electron beam irradiation are similar to the thermal decomposition that occurs during the synthesis of nickel-rich cathode materials with LiOH (Park et al. 2022a). According to Park et al. (2022a), the formation of core-shell-shaped intermediate microstructures depends on the availability of lithium: When the transition metal precursor and lithium precursor can easily come into contact, well-formed nickel-rich-layered structures form at the interface (the lithiation process). However, when there is no lithium precursor present, the thermal decomposition of the TM(OH)₂ leads to the formation of porous structures in the particle core. In contrast to the actual synthesis process of layered cathode materials, electron beam irradiation in TEM does not involve the presence of lithium or heat (at least insignificant). However, the phase evolution that occurs under the electron beam irradiation is similar to the decomposition of $TM(OH)_2$, and the structural defects that form, such as nanopores and cracks, are similar to the intragranular nanopores and intergranular voids that form during the synthesis process.

The phase transition in layered transition metal oxides often goes beyond the formation of the spinel phase. In particular, the layered transition metal oxides used as cathode materials in Li-ion batteries containing nickel can readily change into a rock-salt phase (Hua et al. 2020; Wang et al. 2021). However, a rocksalt phase was not observed in the phase transition of $Co(OH)_2$ when examined using high-resolution TEM or electron diffraction. Both rock-salt cobalt monoxide (CoO, Fm $\overline{3}$ m) and spinel Co₃O₄ (Fd $\overline{3}$ m) are thermodynamically stable phases, and it has been reported that the transition between CoO and spinel Co₃O₄ is reversible (Kong et al. 2019). The rock-salt phase can be oxidized to the spinel phase by annealing at 240 °C under atmospheric pressure of air (Nam et al. 2010), while the reduction process from spinel to rock-salt phase



Fig. 5 a High-resolution TEM image of α-Co(OH)₂ and b HAADF-STEM image of α-Co(OH)₂ after the phase transition to spinel Co₃O₄ was complete

requires a higher temperature of 400 °C under vacuum or very low oxygen partial pressure conditions (Chen et al. 2021; Jang et al. 2019). In the current study, the spinel phase does not undergo any further changes when subjected to a higher e-beam dose or a longer irradiation time. We believe that electron beam irradiation alone is not sufficient to trigger the reduction process from the spinel to the rock-salt phase and that the annealing is necessary for the phase transition to rock salt to occur.

Conclusions

The phase transition of $Co(OH)_2$ from a layered to a spinel structure, induced by electron beam irradiation, was investigated with TEM. The morphology and structural changes were monitored in real time. Both α -Co(OH)₂ and β -Co(OH)₂ underwent a similar phase transition from the layered to the spinel Co₃O₄ structure under the electron beam irradiation. The transformed spinel Co₃O₄ consisted of nanograins with porous morphology. However, α -Co(OH)₂ interacted more sensitively with the e-beam, inducing a faster phase transition and causing a significant volume shrinkage due to the extraction of water molecules. Our findings reveal a comprehensive process which breaks a layered structure and forms nanograins and defects during a phase transition, providing important insight into the phase transition between layered and spinel structures.

Supplementary Information

The online version contains supplementary material available at https://doi. org/10.1186/s40543-023-00395-0.

Additional file 1: Supplementary Information.

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Author contributions

J.H.K. conceived the project and designed the experiments; the samples were grown by K.M.N. and J.Y.P.; X-ray diffraction experiments have been carried out by Y.K.; TEM and SEM experiments have been carried out by J.H.S. and J.H.J.; data analysis has been done by J.H.K. and J.H.S.; the manuscript has been written by J.H.K. and J.H.S., collecting feedback from all the authors.

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Availability of data and materials

The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

Competing interests

The authors declare that they have no competing interests.

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References

Amou M, Larhrib B, Saadoune I. Controlled synthesis of

- Li_{1.17}Ni_{0.21}Mn_{0.54}Co_{0.08}O₂ as a cathode material for Li ion batteries. J Electroanal Chem. 2021;881:114957.
- Chen X, van Gog H, van Huis MA. Transformation of Co_3O_4 nanoparticles to CoO monitored by *in situ* TEM and predicted ferromagnetism at the Co_3O_4/CoO interface from first principles. J Mater Chem c. 2021;9(17):5662–75.
- Deliens M, Goethals H. Polytypism of heterogenite. Mineral Mag. 1973;39(302):152–7.
- Hu Z-A, Xie Y-L, Wang Y-X, Xie L-J, Fu G-R, Jin X-Q, et al. Synthesis of α-cobalt hydroxides with different intercalated anions and effects of intercalated anions on their morphology, basal plane spacing, and capacitive property. J Phys Chem C. 2009;113(28):12502–8.
- Hua W, Wang K, Knapp M, Schwarz B, Wang S, Liu H, et al. Chemical and structural evolution during the synthesis of layered Li(Ni Co, Mn)_o2 oxides. Chem Mater. 2020;32(12):4984–97.
- Huang C-W, Kuo S-S, Hsin C-L. Electron-beam-induced phase transition in the transmission electron microscope: the case of VO_2 (B). CrystEngComm. 2018;20(43):6857–60.
- Ishimaru M, Bae I-T, Hirotsu Y. Electron-beam-induced amorphization in SiC. Phys Rev B. 2003;68(14): 144102.
- Ismail J, Ahmed MF, Kamath PV, Subbanna GN, Uma S, Gopalakrishnan J. Organic additive-mediated synthesis of novel cobalt(II) hydroxides. J Solid State Chem. 1995;114(2):550–5.
- Jang KY, Ahn SJ, Kwon J-H, Nam KM, Kim YH. Novel route from a wurtzite to a rock-salt structure in CoO nanocrystals: in situ transmission electron microscopy study. J Phys Chem C. 2019;123(16):10689–94.
- Jayashree RS, Kamath PV. Electrochemical synthesis of α-cobalt hydroxide. J Mater Chem R Soc Chem. 1999;9(4):961–3.
- Jia Y, Zhang L, Gao G, Chen H, Wang B, Zhou J, et al. A heterostructure coupling of exfoliated Ni–Fe hydroxide nanosheet and defective graphene as a bifunctional electrocatalyst for overall water splitting. Adv Mater. 2017;29(17):1700017.
- Jiang T-T, Wang J-J, Lu L, Ma C-S, Zhang D-L, Rao F, et al. Progressive amorphization of GeSbTe phase-change material under electron beam irradiation. APL Mater. 2019;7(8): 081121.
- Kim H, Choi WI, Jang Y, Balasubramanian M, Lee W, Park GO, et al. Exceptional lithium storage in a Co(OH)₂ anode: hydride formation. ACS Nano. 2018;12(3):2909–21.
- Kong F-C, Li Y-F, Shang C, Liu Z-P. Stability and phase transition of cobalt oxide phases by machine learning global potential energy surface. J Phys Chem C. 2019;123(28):17539–47.
- Li J, Li Z, Zhan F, Shao M. Phase engineering of cobalt hydroxide toward cation intercalation. Chem Sci. 2021;12(5):1756–61.
- Liu Z, Ma R, Osada M, Takada K, Sasaki T. Selective and controlled synthesis of α and β -cobalt hydroxides in highly developed hexagonal platelets. J Am Chem Soc. 2005;127(40):13869–74.
- Ma H, He J, Xiong D-B, Wu J, Li Q, Dravid V, et al. Nickel cobalt hydroxide @ reduced graphene oxide hybrid nanolayers for high performance asymmetric supercapacitors with remarkable cycling stability. ACS Appl Mater Interfaces. 2016;8(3):1992–2000.
- Ma R, Liu Z, Takada K, Fukuda K, Ebina Y, Bando Y, et al. Tetrahedral Co(II) coordination in α-type cobalt hydroxide: rietveld refinement and X-ray absorption spectroscopy. Inorg Chem. 2006;45(10):3964–9.
- Nam KM, Shim JH, Han D-W, Kwon HS, Kang Y-M, Li Y, et al. Syntheses and characterization of wurtzite CoO, rocksalt CoO, and spinel Co₃O₄ nanocrystals: their interconversion and tuning of phase and morphology. Chem Mater. 2010;22(15):4446–54.

- Parajuli P, Park H, Kwon BJ, Guo J, Key B, Vaughey JT, et al. Direct observation of electron beam-induced phase transition in MgCrMnO₄. Chem Mater. 2020;32(24):10456–62.
- Park H, Park H, Song K, Song SH, Kang S, Ko K-H, et al. In situ multiscale probing of the synthesis of a Ni-rich layered oxide cathode reveals reaction heterogeneity driven by competing kinetic pathways. Nat Chem. 2022;14(6):614–22.
- Park JY, Kim HY, Kim Y-I, Jo SY, Abbas SA, Seo D, et al. Chemical and electrochemical synthesis of cobalt hydroxides: selective phase transformation and application to distinct electrocatalytic reactions. J Mater Chem a. 2022;10(22):12047–54.
- Park K-J, Jung H-G, Kuo L-Y, Kaghazchi P, Yoon CS, Sun Y-K. Improved cycling stability of Li[Ni_{0.90}Co_{0.05}Mn_{0.05}]O2 through microstructure modification by boron doping for li-ion batteries. Adv Energy Mater. 2018;8(25):1801202.
- Qian G, Zhang Y, Li L, Zhang R, Xu J, Cheng Z, et al. Single-crystal nickel-rich layered-oxide battery cathode materials: synthesis, electrochemistry, and intra-granular fracture. Energy Storage Mater. 2020;27:140–9.
- Rajamathi M, Kamath PV, Seshadri R. Chemical synthesis of α-cobalt hydroxide. Mater Res Bull. 2000;35(2):271–8.
- Tian L, Zhu JL, Chen L, An B, Liu QQ, Huang KL. Synthesis and characterization of α-cobalt hydroxide nanobelts. J Nanoparticle Res. 2011;13(8):3483–8.
- Vilá RA, Momeni K, Wang Q, Bersch BM, Lu N, Kim MJ, et al. Bottom-up synthesis of vertically oriented two-dimensional materials. 2D Mater. 2016;3(4):041003.
- Wang C, Han L, Zhang R, Cheng H, Mu L, Kisslinger K, et al. Resolving atomicscale phase transformation and oxygen loss mechanism in ultrahighnickel layered cathodes for cobalt-free lithium-ion batteries. Matter. 2021;4(6):2013–26.
- Yang X, Nitta S, Pristovsek M, Liu Y, Liao Y, Kushimoto M, et al. Scalable synthesis of multilayer h-BN on AlN by metalorganic vapor phase epitaxy: nucleation and growth mechanism. 2D Mater. 2019;7(1):015004.
- Yao L, Majumdar S, Äkäslompolo L, Inkinen S, Qin QH, van Dijken S. Electron-beam-induced perovskite–brownmillerite–perovskite structural phase transitions in epitaxial La_{2/3}Sr_{1/3}MnO₃ films. Adv Mater. 2014;19(26):2789–93.
- Ye S-H, Shi Z-X, Feng J-X, Tong Y-X, Li G-R. Activating CoOOH porous nanosheet arrays by partial iron substitution for efficient oxygen evolution reaction. Angew Chem Int Ed. 2018;57(10):2672–6.

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