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Pulverization-Tolerant CuSe Nanoflakes with High (110) Planar Orientation for High-Performance Magnesium Storage

Yuexing Zhang, Youqi Zhu, Zhitao Wang, Hui Peng, Xinyu Yang, Yuehua Cao, Changliang Du, Xilan Ma, and Chuanbao Cao**

Copper chalcogenides are of great interest as conversion-type cathode materials due to their large specific capacity for rechargeable magnesium batteries, yet are subjected to severe capacity fading brought about by structure collapse in repetitive charge–discharge cycling. Herein, single-crystalline and (110) preferentially oriented CuSe nanoflakes are designed via a temperature-controlled crystal growth route under microwave irradiation. The as-prepared CuSe nanoflake cathode materials can present high reversible capacity (204 mAh g^{-1} at 200 mA g^{-1} current density), outstanding rate capability, and remarkable long-term cycling stability (≈0.095% capacity decay per cycle at 1 A g^{-1} within 700 cycles). The multistep reversible conversion mechanism of the CuSe nanoflake cathode materials is evidenced by ex situ X-ray photoelectron spectroscopy and X-ray diffraction. Structure evolution investigation suggests that the single-crystalline CuSe nanoflakes can exhibit relatively durable structural stability. The desirable cycling stability can be ascribed to the excellent pulverization-tolerance of the CuSe nanoflake cathode materials endowed by the multistep reversible conversion mechanism and the single-crystalline feature. Furthermore, the preferentially-oriented (110) active plane is favorable for electrochemical reactions to ensure high specific capacity. This work can afford a crystal engineering strategy to fabricate high-performance conversion-type electrode materials for rechargeable magnesium batteries.

1. Introduction

Rechargeable magnesium batteries (rMBs) are prospective candidates for sustainable energy storage systems and have drawn considerable interest in recent years owing to high energy density, sufficient magnesium availability, and operating safety.[1] Developing suitable and effective cathode materials is the fundamental technology to satisfy the rapid progression of rMBs.[2] Recently, the conversion-type cathode materials, such as AgCl,[3] CoS,[4] NiS$_x$,[5] CuS,[6] Cu$_2$Se,[7] Cu$_{2-x}$Se,[8] and CuSe,[9] have captured extensive attention owing to their high theoretical capacity provided by multiple oxidation states.[10] Especially, copper selenide (CuSe) is considered as a promising cathode material with high reversible specific capacity.[7,9,11] However, most conversion-type cathode materials generally suffer from sharp capacity degradation and undesirable cycling performance owing to the structure collapse brought by large Columbic interaction between divalent Mg^{2+} ion and host lattice, the pulverization of active materials triggered by crystallographic transformations,[8] the rearrangement of surface structure produced by electrolyte corrosion,[12] and the huge volume expansion by in-depth magnetization reaction.[10,13] To address the aforementioned problems, tremendous efforts have been dedicated to enhancing structural durability and pulverization-tolerance of these conversion-type cathode materials, such as introducing flexible matrix with small volume effect,[14] substituting host anions with more polarizable and much larger guest atoms,[15] and cutting-down particle size to nanoscale level.[16] However, the most reported cathode materials with structural and component modifications are subject to complex and uncontrollable synthesis processes. Additionally, nanomaterials with single and primary structure usually tend to aggregate into irregular particles upon cycling, leading to fast capacity degradation and short cycle life.[9] The rational design of metal chalcogenide cathode materials is beneficial to improve the performance of rMBs.[17] Therefore, it is highly required to exploit talented cathode materials with good intrinsic electrochemical activity and long-term cycling stability for rMBs.

The crystal engineering of electrode materials is a powerful technique to control their intrinsic activity for battery application. Recently, single-crystalline electrode materials have

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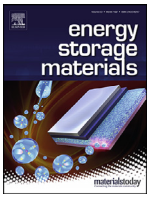

Tuning oxygen redox chemistry of P2-type manganese-based oxide cathode via dual Cu and Co substitution for sodium-ion batteries

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ABSTRACT

High-voltage layered Mn-based oxide is promising high-capacity cathode via exploiting the oxygen redox chemistry. But such redox often suffer from irreversible oxygen loss, leading to severe voltage hysteresis, particle cracking and capacity decay. Hence, the complementary strategy of dual Cu and Co substitution is revealed to stabilizing the anion redox chemistry of P2-$Na_{2/3}$(Mn-Ni-Cu-Co)O_2 cathode under upper cut-off voltage. Dual substitution with Cu for Mn and Co for Ni forms stable Cu-O and Co-O octahedrons, which modulate the lattice structure with the shrinkage of TMO_2 sheets and expansion of Na layer spacing to enhance the Na^+ diffusion kinetics. Co substitution can raise high voltage region to tune the cut-off voltage up to 4.3 V and activate oxygen redox to weaken irreversible O_2 loss. And Cu substitution can inhibit the O_2 loss and suppress the voltage decay via the interaction between Cu 3d and O 2p orbitals. The P2-type $Na_{0.67}Mn_{0.6}Ni_{0.2}Cu_{0.1}Co_{0.1}O_2$ cathode induced by the complementary effect can boost long cycling life (82.07% capacity retention after 500 cycles) and remarkable rate capability under high upper cut-off voltage in half-cell. Furthermore, the full cells also exhibit outstanding rate capability with a high discharge capacity of 62.6 mAh g^{-1} at 20 C.

1. Introduction

Sodium-ion batteries (SIBs) open up a great possibility for practical application to replace current lithium-ion batteries (LIBs) due to their similar “rocker chair” principle with LIBs, earth-abundant and low-cost sodium source as well as universal cheap Al collector for both cathode and anode [1-4]. The layered Mn-based oxide cathode promises great potential as Na^+ host materials because of abundant resource, low cost and environmental friendliness of Mn species, simple preparation process and high specific capacity [2,5-8]. According to sodium ion occupying sites and O sequence, the layered Mn-based oxide cathode is commonly divided into two categories: P2- and O3-type oxide cathode [4,9]. P2-type cathode holds much greater advantages in phase transition, air stability, ion conductivity and Na^+ diffusion kinetics compared with O3-type one [10,11]. Particularly, like Li-rich cathode in LIBs, P2-type Mn-based oxide cathode can generally provide high specific capacity through the anionic redox reaction with the cut-off voltage beyond 4.2 V [12-21]. However, along with the reversible anionic redox processes (O^{2-}/O_2^{n-}), the irreversible O_2 loss is inevitable that could bring about unstable structure evolution and particle cracking, which can cause cycling stability deterioration and voltage hysteresis aggravation [16]. Besides, P2-type Mn-based oxide cathode is also confronted with Jahn-teller effect, interface instability and phase transition under high voltage [11,19,22-31].

Heteroatom substitution, such as Li, Mg, Zn, Ti, Al etc., has been widely employed to resolve the aforementioned issues, which can bring forward tailorable compositional diversity and complex structural chemistry to adjust crystal structure, Na^+ ion conductivity, phase transition and the irreversible oxygen redox to ensure tunable electrochemical performance [25,32-43]. Xiao et al. proposed that $Na_{2/3}Ni_{1/6}Mn_{2/3}Cu_{1/9}Mg_{1/18}O_2$ cathode with the optimal morphology and structure modulation could display excellent electrochemical performance with tailoring voltage below 4.2 V [38]. Kong et al. reported that Cu/Mg co-doping in P2-$Na_{0.67}Mn_{0.75}Ni_{0.25}O_2$ can modify the lattice structure and improve the reversibility of anionic redox, but the cycling stability also depends on clipping voltage below 4.2 V [32]. Based on heteroatom substitution, tailoring voltage does avoid the capacity fading and voltage decay caused by irreversible oxygen redox, but the

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Anionic Se-Substitution toward High-Performance $CuS_{1-x}Se_x$ Nanosheet Cathode for Rechargeable Magnesium Batteries

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Rechargeable magnesium batteries (rMBs) are promising as the most ideal further energy storage systems but lack competent cathode materials due to sluggish redox reaction kinetics. Herein, developed is an anionic Se-substitution strategy to improve the rate capability and the cycling stability of 2D $CuS_{1-x}Se_x$ nanosheet cathodes through an efficient microwave-induced heating method. The optimized $CuS_{1-x}Se_x$ ($X = 0.2$) nanosheet cathode can exhibit high reversible capacity of 268.5 mAh g^{-1} at 20 mA g^{-1} and good cycling stability (140.4 mAh g^{-1} at 300 mA g^{-1} upon 100 cycles). Moreover, the $CuS_{1-x}Se_x$ ($X = 0.2$) nanosheet cathode can deliver remarkable rate capability with a reversible capacity of 119.2 mAh g^{-1} at 500 mA g^{-1}, much higher than the 21.7 mAh g^{-1} of pristine CuS nanosheets. The superior electrochemical performance can be ascribed to the enhanced reaction kinetics, enriched cation storage active sites, and shortened ion diffusion pathway of the $CuS_{1-x}Se_x$ nanosheet. Therefore, tuning anionic chemical composition demonstrates an effective strategy to develop novel cathode materials for rMBs.

Rechargeable magnesium batteries (rMBs) have been identified as an attractive alternative to the commercialized lithium-ion batteries due to the dendrite-free metallic Mg anode, natural abundance of magnesium resources, and higher specific volumetric capacity (3833 mAh cm^{-3}) as compared to that of lithium counterparts (2046 mAh cm^{-3}).[1] Currently, the development of capable cathode materials with high energy density and long-term cycling stability is highly required for rMBs. Various host materials, including metal oxides (V_2O_5,[2] VO_x,[3] MnO_2,[4] and MoO_3[5]), metal sulfides (Mo_6S_8,[6] MoS_2,[7] Ti_2S_4,[8] α-Ag_2S,[9] VS_4,[10] and VS_2[11]), metal selenides (Mo_6Se_8,[12] $TiSe_2$,[13] Cu_2Se,[14] and $Ni_{0.75}Fe_{0.25}Se_2$[15]), have been proposed as possible cathode candidates. In particular, copper sulfide (CuS) has recently attracted great attention because of its unique properties of nontoxicity, eco-friendliness, low cost, and high theoretical specific capacity (560 mAh g^{-1}).[16] Nevertheless, CuS cathode materials are still subject to a series of unsatisfactory performances related to reversible capacity, rate capability, and cycling stability caused by the serious polarization from divalent Mg^{2+}.[17] Thus, the development of suitable host materials with fast reaction kinetics is highly desired but still challenging.

To solve the aforementioned issues, many strategies have been proposed and brought considerable achievement in CuS cathode materials, including: i) increased ionic diffusion kinetics through elevating working temperature,[16] ii) enhanced Mg^{2+} mobility by adjusting electrode–electrolyte interface,[18] and iii) shortened Mg^{2+} diffusion length via constructing suitable nanoarchitectures.[19] However, the electron and solid-state Mg^{2+} transport kinetics of the most reported CuS cathode materials are still unsatisfactory. It is therefore a great challenge to effectively design CuS cathode materials with high practical capacity and long cycling life, especially at high current densities. In our previous work,[19a] although the hierarchical CuS nanosheet showed good cycling performances for rMBs (135 mAh g^{-1} at 200 mA g^{-1} upon 200 cycles), its rate capability still needs to be further improved. Heavy heteroatom substitution in transition metal sulfides is expected as an efficient route to regulate their atomic structure for providing optimized configuration for Mg^{2+} uptake.[20] In particular, the fractional anionic Se-substitution to S could enlarge the Mg^{2+} diffusion path and reduce their interaction with the based lattice, thereby cutting down the ionic diffusion barrier and resulting much better kinetics.[21] Till now, despite the well-known Chevrel phase $Mo_6S_{8-X}Se_X$ ($X = 0, 1, 2$),[12,21a,22] Se-substituted copper sulfide cathode materials for rMBs have been rarely reported.

Herein, we develop an efficient synthesis strategy to prepare 2D anionic Se-substituted $CuS_{1-x}Se_x$ nanosheets with about

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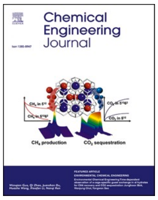

High-valence Ni and Fe sites on sulfated NiFe-LDH nanosheets to enhance O-O coupling for water oxidation

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ABSTRACT

High-valence Ni and Fe metal sites have demonstrated a crucial role in enhancing the catalytic performances of NiFe-LDH electrocatalysts in oxygen evolution reaction (OER). Although considerable OER catalytic performances achieved under high overpotential, the catalytic talent of NiFe-LDH electrocatalysts at low overpotential is rarely realized due to the absence of high-valence Ni and Fe sites. We herein report a surface engineering route to fabricate sulfated NiFe-LDH nanosheets via ion exchange strategy in sulfate-rich media. XPS results reveal a modified surface electronic structure with high-valence Ni and Fe after ion exchange reaction. Computational PDOS results suggest that computed d-band centers (ε_d) of Fe and Ni for sulfated NiFe-LDH show a significant downward shift resulting an increased valence of metal cation with orbital volume shrinkage. The high-valence Fe can facilitate a optimized multi-electron process of Ni center from $[Ni^{II}\text{-}OH]^-/[Ni^{III}\text{-}OH]^-$ to $Ni^{IV}\text{-}OOH$ rather than Ni^{II}/Ni^{III} to Ni^{IV} at low overpotential. The high-valence Ni can serve as the highly active center for O-O coupling during OER process. Combined with the synergetic action of high-valence Fe and Ni, the sulfated NiFe-LDH nanosheets exhibit much larger reaction kinetics and outstanding electrocatalytic activity on glassy carbon electrode ($\eta_{10} = 219$ mV, $\eta_{50} = 288$ mV) with a remarkable long-term stability.

1. Introduction

Harvesting electrical energy from renewable sources and converting it into chemical energy by water splitting are viewed as promising pathway to address the energy challenge [1-11]. However, the conversion efficiency is highly depended on the kinetics of the involved oxygen evolution reaction (OER) half-reaction, which is related to four proton-coupled electron charge transfer steps, and requires a substantial extra potential to proceed even with noble catalysts including RuO_2 and IrO_2 [12-17]. Therefore, immense efforts have been made to emerge highly efficient and abundant OER catalysts. Layered double hydroxides (LDHs) have demonstrated a promising OER catalytic activity benefiting from versatile combinations of metal cations (Fe, Co, Ni, Mn, etc.) and a unique layered structure where the appropriate interlayer spacing accelerates the diffusion of active species to the abundant active sites [18-21]. Particularly, NiFe-LDH is recognized as the best OER material due to the favorable electronic structure of cationic metals [22-25].

Discovering the in-depth catalytic mechanism of NiFe-LDH is of great importance to further boost its performances. Ram Subbaraman *et al.* exhibited that the OER activity of these 3d-M hydr(oxy)oxide systems follows the Ni > Co > Fe > Mn order using the $OH_{ad}\text{–}M^{2+\delta}$ interaction as the primary descriptor [26]. Heteroatomic Fe doping into pristine nickel hydroxide can significantly improve its OER activity [27-30]. Subsequently, great efforts have been made to investigate the catalytic mechanism of Ni-Fe materials evolving from pristine Ni or Fe to Ni-Fe LDHs with synergetic effect [28-33]. The monitoring on the chemical state changes of NiFe-based catalysts is also powerful for understanding of Ni and Fe roles in the reaction mechanism. Jamie Y. C. Chen *et al.* reported that Fe^{IV} species are detected in NiFe oxyhydroxide catalyst during steady-state water oxidation and occupy edge/corner or lattice defect of NiOOH [30]. Researchers also revealed that NiFe-based catalysts would undergo a phase-transformation into γ-NiOOH with

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High-voltage P2-type manganese oxide cathode induced by titanium gradient modification for sodium ion batteries

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HIGHLIGHTS

- P2-type manganese oxide cathode combines high operating voltage and anionic redox.
- Ti gradient modification achieves Ti-enriched surface and Ti-substituted interior.
- Gradient modification enhances interfacial stability to reduce side reactions.
- Gradient modification mitigates phase transition and irreversible oxygen activity.
- Excellent electrochemical performance is obtained at 4.7 V high operating voltage.

ARTICLE INFO

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Titanium gradient modification
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ABSTRACT

Constructing layered high-voltage P2-type manganese oxide with working voltage above 4.5 V incorporating into $Ni^{2+/4+}$ redox and high capacity based on anionic redox has become trend to develop high energy density sodium ion batteries. However, capacity fading and undesired rate capability caused by serious phase transition, irreversible oxygen activity and electrolyte/electrode side reactions would occur especially under high operating voltage besides the Jahn-Teller effect. Here, based on anionic and cationic redox, a novel titanium gradient modification coupling with the synergic Ti-enriched surface and Ti-substituted interior is proposed to achieve excellent stability and rate capability. As a result, the high-voltage P2-$Na_{0.66}Mn_{0.54}Ni_{0.13}Co_{0.13}O_2$ cathode induced by titanium gradient modification can deliver a large reversible discharge capacity of 133.2 mA h g^{-1} with 77.9% capacity retention after 100 cycles under 4.7 V cut-off voltage at 1C (200 mA g^{-1}), and achieve a high energy density of 456.4 Wh kg^{-1}. These outstanding results are attributed to the facts that Ti gradient modification not only is beneficial for suppressing the side reactions and enhancing the interfacial conductivity, but also can modify the lattice structure to improve the structural stability, leading to mitigate the phase transition and irreversible oxygen activity.

1. Introduction

With significantly increased demand for large-scale energy storage systems, sodium ion batteries (SIBs) are emerging as promising post lithium-ion battery candidates due to abundant sodium resources, low cost and similar electrochemical reactions [1–12]. However, the application of SIBs has been greatly restricted, especially for cathode material to a certain extent, because Na^+ (1.02 Å) ions have larger ionic radius than Li^+ (0.76 Å) ions [5,6,8]. Among layered metal oxide, olivine phosphates, sodium super ionic conductor (NASICON), Prussian blue analogs, and fluorophosphates, layered metal oxides (Na_xTMO_2) as universal research candidate are mainly reflected in P2- and O3-type cathode with fast 2D Na^+ ions diffusion channel [13–20]. P2-type manganese oxide cathode has more advantages than O3-type because of its better theoretical capacity, structural reversibility and air stability [21]. However, the rapid capacity fading and poor rate capability owing to its undesired morphological characteristics is still insufficient for energy storage applications [22–25].

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Constructing sheet-assembled hollow CuSe nanocubes to boost the rate capability of rechargeable magnesium batteries†

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Copper selenide has been considered as a much more promising conversion-type cathode material for rechargeable magnesium batteries than copper sulfide because of its better conductivity. However, the magnesium ion diffusion in the lattice of the CuSe host is subject to a great coulombic resistance due to the relatively high charge density and ion polarization of the divalent Mg^{2+}, leading to undesired rate capability and low reversible capacity. Herein, a morphology engineering strategy is presented to construct sheet-assembled hollow CuSe nanocubes by a simple template-directed selenation reaction at room temperature. Electrochemical measurements suggest that the CuSe nanocubes could exhibit an ultra-high initial discharge capacity of 596 mA h g^{-1} and maximum specific capacity of 252 mA h g^{-1} and maintain a relatively high reversible capacity of 170 mA h g^{-1} after 100 cycles at 200 mA g^{-1}. Furthermore, a remarkable rate capability could be obtained with 77.6 mA h g^{-1} discharge capacity at 5 A g^{-1}. Additionally, the CuSe nanocubes exhibit excellent compatibility with $Mg(BH_4)_2/(CF_3)_2CHOH/$DME electrolyte and follow a two-step conversion mechanism. Such superior magnesium storage properties demonstrate that constructing a hierarchical hollow structure could be one of the effective methods to promote the magnesium storage kinetics of CuSe cathode materials.

Introduction

Rechargeable magnesium batteries (rMBs) have been recognized as one of the most promising energy storage devices in the post-LIB era due to the low-cost, enhanced safety and ultra-high theoretical volumetric capacity (3383 mA h cm^{-3}) of the abundant magnesium metal in the earth's crust (2.9%, about 10^4 times higher than 0.002% of Li).[1–4] However, the magnesium ion diffusion in the lattice of the cathodes and the magnesiation/demagnesiation reactions suffer from a great coulombic resistance and a high energy barrier, respectively, due to the relatively high charge density and ion polarization of the divalent Mg^{2+}, leading to a sluggish reversibility of the magnesium storage mechanism. Therefore, it is of great importance to develop new types of high-reversibility cathode materials for rMBs.[5–7] After the first report of the Chevrel phase cathode by Aurbach in 2000,[8] several intercalation-type cathode materials have been investigated, such as V_2O_5,[9,10] MnO_2 (ref. 11–13) and MoS_2.[14,15] Unfortunately, the reported cathode materials usually show rather low specific capacity and inferior rate performance due to the sluggish Mg^{2+} transport kinetics and limited Mg^{2+} storage sites. Therefore, it is still highly desired to develop new efficient cathode materials.

Conversion-type cathode materials have caught extensive attention in recent years on account of their relatively higher capacity. Copper-based chalcogenides, especially copper sulfide, have been widely investigated as typical conversion-type cathode materials.[16–23] However, the low conductivity of CuS causes high joule heat in the repeated charge and discharge processes, which greatly reduces its structural stability and thus leads to poor cycling stability and rate capability.[24] Recently, CuSe has shown great promise due to its good conductivity and the weak electronegativity and the large ionic radius of Se.[25,26] In 2019, our group found that CuSe nanoparticles could show high specific capacity but undesirable rate capability and cycling stability.[27] Additionally, our work also suggested that anionic Se-substitution towards CuS nanosheets could improve the rate capability.[28] Chen *et al.* constructed nanosheet-assembled hierarchical starfish-like $Cu_{2-x}Se$ that could show a good cycling stability.[29] Therefore, the construction of a reasonable hierarchical structure has a significant effect on the electrochemical magnesium storage performance of the cathode material, which could originate from the fact that the special multistage structure not only inherits the advantages of a single

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Advances and challenges in metal–organic framework derived porous materials for batteries and electrocatalysis

Liqin Wang, Youqi Zhu,* Changliang Du, Xilan Ma and Chuanbao Cao *

The development of advanced functional materials is of great significance for applications in energy storage and conversion fields. Metal–organic framework (MOF) derived porous materials have attracted extensive attention due to their high porosity, complex components and controllable structures. Although considerable achievements have been made in the controllable synthesis of multifunctional MOF derivatives, their systematic synthesis and applications in new-style energy storage and conversion devices (*e.g.* sodium ion batteries, potassium ion batteries, zinc ion batteries and fuel cells) have rarely been reviewed in depth. Given that materials' structures are highly dependent on the particular synthetic strategy and determine the final physical and chemical performances, a comprehensive insight into the latest advances in complex MOF-derived porous materials is provided in this review. The versatile architectures of functional materials and their influences on properties are clearly summarized. The advantages of the MOF-derived route over traditional non-MOF methods are highlighted. In the end, the challenges and the prospective research direction of MOF-derived functional materials in energy storage and conversion fields are proposed. The strategy–structure–property relationships in this review will provide scientific evidence on the reasonable design of high-efficiency MOF-derived functional materials for new energy systems.

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1. Introduction

As a result of the increasing energy demand and environmental degradation caused by the huge consumption of fossil fuels, exploring new energy and renewable resources is extremely urgent.[1–3] Developing energy storage and conversion technologies, such as rechargeable batteries, water splitting, and fuel cells, is an essential part of achieving environmental sustainability.[4–8] However, the development of traditional graphite anodes and precious metal electrocatalysts (Pt, Au, IrO_2, and RuO_2) is limited. Exploring new-style technologies to obtain

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Engineering yolk–shell P-doped NiS_2/C spheres *via* a MOF-template for high-performance sodium-ion batteries†

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Transition metal sulfides generally demonstrate unsatisfactory capacity and a limited rate capability that still restrict their application for sodium-ion batteries. Herein, yolk–shell P-doped NiS_2/C spheres were synthesized *via* a Ni-MOF template with phytic acid acting as a P source to significantly enhance the sulfide's sodium storage property. The yolk–shell P-doped NiS_2/C spheres exhibited an ultrahigh initial discharge and charge capacities of 3546.7 and 2622.9 mA h g^{-1} with 72.9% coulombic efficiency, and maintained a relatively high reversible capacity of 1113.5 mA h g^{-1} at 0.1 A g^{-1} after 20 cycles. Electrochemical measurements further revealed that the yolk–shell P-doped NiS_2/C spheres could also deliver a good rate capability and stable long-term cycling performance with 766.8 mA h g^{-1} reversible capacity at 0.5 A g^{-1} after 400 cycles. The satisfactory electrochemical results could be ascribed to the confinement and synergistic effect from the robust yolk–shell framework and heteroatom P doping. Therefore, it was demonstrated that morphology tuning and heteroatom P doping can serve as effective strategies to significantly improve the electrochemical properties of transition metal sulfides for sodium-ion batteries.

Introduction

Layered transition metal sulfides have attracted considerable attention as novel anode materials for sodium-ion batteries (SIBs) as they offer much better mechanical stability, electronic conductivity, and gravimetric energy density as well as richer redox reaction sites compared to nongraphitic carbon (<300 mA h g^{-1}).[1–4] In addition, the low electronegativity of the S atom, the weak metal–sulfur bonding, and the discharge Na_2S product can generate better reaction kinetics to intensify the sodiation/desodiation process compared to that of the corresponding metal oxide counterparts.[5–7] NiS_2 has been widely investigated due to its four-electron conversion reaction ($NiS_2 + 4Na^+ + 4e^- \leftrightarrow Ni + 2Na_2S$) and a much higher theoretical capacity of 873 mA h g^{-1} compared to other nickel sulfides (~591 mA h g^{-1} of NiS and ~446 mA h g^{-1} of Ni_3S_2).[8,9] However, NiS_2 also suffers from intrinsic sluggish kinetics and a large volume variation same as other metal sulfides, so it is a great challenge to develop effective techniques to solve these problems.[10,11]

Constructing nanostructures by a freestanding nanosheet and/or hollow or yolk–shell skeleton for electrode materials is a promising strategy to improve their reaction kinetics.[9,12,13] Many strategies have been proposed to fabricate a yolk–shell framework, such as carbon coating and the template-assisted technique.[6,14,15] However, most of the reported methods are time-consuming and material-wasteful. Metal–organic frameworks (MOFs) have been demonstrated to be effective candidates to construct a porous yolk–shell structure with a high surface area and ordered pore dispersion.[16,17] The coordinated metal species can be converted into metallic nanocrystals and then to various metal sulfides.[18,19] Additionally, the organic linkers are translated into a carbon skeleton to enhance the conductivity of the active material.[20–23] Zhang reported hollow NiS_2 spheres prepared by Ni-MOFs with a capacity of 848 mA h g^{-1} at 0.1 A g^{-1} for SIBs.[24] Furthermore, yolk–shell frameworks possess a much greater confinement effect in comparison with hollow spheres. The shell can be modified by functional groups to increase the exposed active sites and protect the stability of the yolk. An appropriate void space can effectively buffer large volume variations to maintain the original structure and further achieve prolonged cycling life.[6,14]

Heteroatom doping (*i.e.*, N, B, S, P elements) can further enhance the specific capacity and rate capability *via* a synergistic effect in yolk–shell hybrids.[2,25–27] The intercalated P atoms can not only enlarge the *d*-spacing of active materials to enhance electron/ions transport but can also produce rich defects to adjust the Na-ions insertion energy and improve the

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Cuprous Self-Doping Regulated Mesoporous CuS Nanotube Cathode Materials for Rechargeable Magnesium Batteries

Changliang Du, Youqi Zhu,* Zhitao Wang, Liqin Wang, Waqar Younas, Xilan Ma, and Chuanbao Cao*

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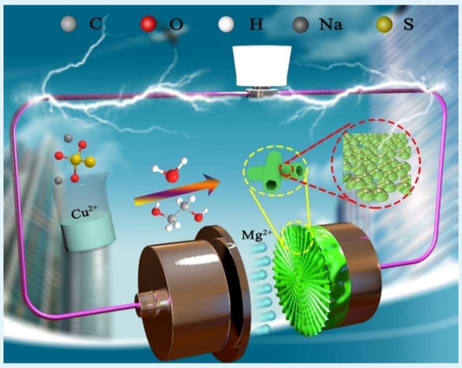
ABSTRACT: Copper sulfides are broadly explored as the possible cathode materials for rechargeable magnesium batteries on account of their high theoretical capacity of 560 mAh g^{-1}. However, the CuS cathodes usually suffer from serious capacity decay caused by structure collapse during the repeated magnesiation/demagnesiation process. Herein, we present a cuprous self-doping strategy to synthesize mesoporous CuS nanotubes with robust structural stability for rechargeable magnesium batteries and regulate their electrochemical magnesium storage behavior. Electrochemical results show that the mesoporous CuS nanotubes can exhibit high specific capacity, remarkable cycling performance, and good rate capability. The observed discharge capacity of the mesoporous CuS nanotubes could reach about 281.2 mAh g^{-1} at 20 mA g^{-1} and 168.9 mAh g^{-1} at 500 mA g^{-1}. Furthermore, a remarkable ultralong-term cyclic stability with a reversible capacity of 72.5 mAh g^{-1} at 1 A g^{-1} is obtained after 550 cycles. These results demonstrate that the mesoporous nanotube structure and the simple cuprous self-doping effect could promote the practical application of copper sulfide cathode materials for rechargeable magnesium batteries.



KEYWORDS: *self-doping, CuS nanotubes, cathode, rechargeable magnesium batteries, electrochemical magnesium storage*

1. INTRODUCTION

Rechargeable magnesium batteries (rMBs) are the promising energy storage device for large-scale power plant due to the cost-effective property, enhanced safety, and high theoretical energy density of the earth-abundant magnesium metal anode.[1−3] However, their commercial application is obstructed by the lack of capable cathode materials. Therefore, it is urgent to discover an ideal cathode material. After the first proposed Chevral phase cathode by Aurbach's group,[4] several types of possible candidates have been reported. Among them, transition metal oxides (TMO) and sulfides (TMS) are the most typical candidates, such as MnO_2,[5−7] V_2O_5,[8,9] MoO_3,[10] MoS_2,[11,12] TiS_2,[13,14] and VS_x.[15,16] Unfortunately, none of these cathode materials can simultaneously demonstrate an ideal specific capacity and remarkable cycling stability. As one of transition metal sulfides, CuS has already been used in many fields, such as optical limiting,[17] supercapacitor,[18] and photocatalysis.[19−21] Because of its desirable theoretical reversible capacity (560 mAh g^{-1}), CuS has recently attracted great attention as cathode materials for rMBs.[22−26] In 2016, Duffort's group reported that the CuS cathode materials could exhibit a considerable specific capacity of 200 mAh g^{-1} at 150 °C.[23] Unfortunately, the undesirable room-temperature electrochemical property and the long-time pre-activation process have limited its further development. On this basis, Mai's group developed CuS particles that have good electrochemical properties at room temperature. However, it just shows undesired cycling stability.[24] In 2019, Wang et al. reported CuS nanosheets that could show remarkable reversible capacity and relatively high cycling performance but a poor rate performance.[27] After that, Shen et al. reported that the hollow CuS nanocubes could deliver high specific capacity and better tolerance toward high current density.[28]

Therefore, it can be inferred from the above discussion that the morphology of electrode material has a great impact on its electrochemical performance. A variety of CuS with various morphologies have been used in several energy storage systems, such as particles,[24,29−31] spheres,[32,33] nanotubes,[34] nanorods,[35] nanowires,[36] nanosheets,[25,27,37] and nanocubes.[28,38] Among them, the hollow structure could express better electrochemical properties. This superiority can be put down to its lower density, larger surface area, and higher loading capacity.[39,40] Furthermore, hollow structured materials can effectively alleviate the volume expansion caused by the electrochemical reaction process, thus improving the cyclic stability and the rate capability.[41−45] In addition, porous materials can improve electrochemical energy storage by

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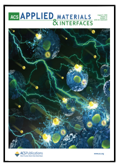

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Mo-Modified P2-type Manganese Oxide Nanoplates with an Oriented Stacking Structure and Exposed {010} Active Facets as a Long-Life Sodium-Ion Battery Cathode

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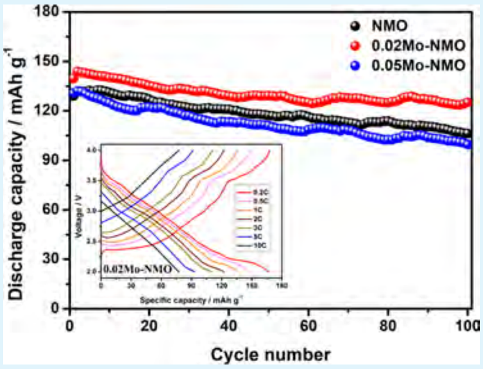
S *Supporting Information*

ABSTRACT: Layered manganese-based cathode materials are of great interest because of their high specific capacities for sodium-ion batteries. However, the Jahn−Teller effect and the inevitable phase transition are detrimental for achieving considerable cycling stability and rate capability. Herein, a P2-type manganese oxide nanoplate cathode material modified by Mo-substitution with an oriented stacking structure and exposed {010} active facets is reported. The manganese oxide nanoplate cathode yields remarkable capacity retention of 86% after 1200 cycles at 10 C (2000 mA g^{-1}). The specific power density is estimated to be as high as 530 W kg^{-1} with a specific discharge capacity 143.9 mA h g^{-1} at 1 C and 89.6% capacity retention up to 100 cycles. The superior electrochemical performances can be attributed to the efficient chemical modification and the unique structural features of the present manganese oxide nanoplate. Mo-modification can endow the manganese oxide cathode with enlarged lattice space and average oxidation state and thus favorable Na^+ diffusion to inhibit the Jahn−Teller effect and improve the structure stability, thereby achieving an extremely long cycling life. A multilayer oriented stacking nanoplate structure with exposed {010} active facets is also beneficial for providing more surface active sites and shortening the Na^+ diffusion path, leading to better rate capability.



KEYWORDS: *Mo-modification, oxidation state, sodium manganese oxide, nanoplates, sodium-ion battery*

1. INTRODUCTION

Sodium-ion batteries are emerging as one of the promising next-generation energy storage devices and have attracted extensive research because of high abundance and low cost of sodium resources, as well as their similar electrochemical behaviors to lithium-ion batteries.[1−4] Great efforts have been dedicated to exploring various novel cathodes, which is of great significance for the development of sodium-ion batteries.[5] Especially, layered multicomponent sodium transition-metal oxide (Na_xTMO_2) are considered as the most promising candidates because of simple manipuility, high theoretical capacity, and favorable two-dimensional Na^+ ions diffusion channel. Recently, P2-type and O3-type Na_xTMO_2 have captured the research interest. In particular, P2-type Na_xTMO_2 have received much more concern because of their lower diffusion barrier, higher ionic conductivity, and smaller hygroscopicity.[4,6−10] Considering the abundant resources, low cost, and environmental friendliness of manganese, P2-type layered sodium manganese-based cathodes have received intensive concern.[11,12] However, the Jahn−Teller distortion induced by Mn^{3+} ion and the drastic phase transformations caused by the larger ionic radius of sodium can cause significant capacity degradation and poor rate capability during the repeated sodium de/intercalation process.[13−16]

In order to solve the aforementioned problems, heteroatom modification has become an effective strategy, which can not only affect the crystal structure to improve the structural stability at a certain extent and adjust the average oxidation state of Mn to suppress the unstable electronic structure of Mn^{3+}, but also enhance the electronic and ionic conductivities of active materials.[17−23] Li and coworkers confirmed that Cu and Mg multimetal substitution can exhibit synergetic effects in $Na_{0.67}Mn_{0.8}Cu_{0.1}Mg_{0.1}O_2$ cathode material for achieving enhanced structural reversibility.[17] Chen et al. reported $Na_{0.44}Mn_{0.6}Ni_{0.4-x}Cu_xO_2$ cathode material doped by inactive copper, which can enlarge lattice space and reduce irreversible

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Cobalt-doping SnS_2 nanosheets towards high-performance anodes for sodium ion batteries†

Liqin Wang, Quanqing Zhao, Zhitao Wang, Yujun Wu, Xilan Ma, Youqi Zhu* and Chuanbao Cao *

Layered SnS_2 is considered as a promising anode candidate for sodium-ion batteries yet suffers from low initial coulombic efficiency, limited specific capacity and rate capability. Herein, we report a cobalt metal cation doping strategy to enhance the electrochemical performance of a SnS_2 nanosheet array anode through a facile hydrothermal method. Benefitting from this special structure and heteroatom-doping effect, this anode material displays a high initial coulombic efficiency of 57.4%, a superior discharge specific capacity as high as 1288 mA h g^{-1} at 0.2 A g^{-1} after 100 cycles and outstanding long-term cycling stability with a reversible capacity of 800.4 mA h g^{-1} even at 2 A g^{-1}. These excellent performances could be ascribed to the Co-doping effect that can increase the interlayer spacing, produce rich defects, regulate the electronic environment and improve conductivity. Besides, a carbon cloth substrate can maintain the integrity of the electrode material framework and buffer its volume variation, thus boosting intrinsic dynamic properties and enhancing sodium storage performance.

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1. Introduction

Layered tin disulfide (SnS_2) has been proposed as one of the most hopeful anode candidates for SIBs because of its high theoretical capacity (1136 mA h g^{-1}) resulting from conversion and alloying reactions ($SnS_2 + 4Na \rightarrow Sn + 2Na_2S$; $Sn + 3.75Na \leftrightarrow Na_{3.75}Sn$).[1] Furthermore, layered SnS_2 can be exfoliated to a single- or few-layered sheet to generate distinctive physical and chemical properties and afford an open framework to facilitate Na-ion transportation and electrolyte flooding.[2–4] Additionally, the large interlayer spacing (0.59 nm) and stable CdI2-type structure with three stacked atom (S–Sn–S) layers united by van der Waals forces of SnS_2 make it a suitable candidate for hosting the Na^+ intercalation.[5,6] However, like other sulfide material electrodes, the SnS_2 anode is also subjected to a large volume variation (520% deriving from Sn to $Na_{3.75}Sn$) and poor electrical conductivity, which could result in severe pulverization and aggregation and thus unsatisfactory electrochemical performances.[7] Various schemes have been implemented to overcome the aforementioned challenges, such as constructing special morphologies (porous or hollow structure), heteroatom doping and introducing conductive substrates.[8–11] Hybridizing SnS_2 with a conductive matrix is an effective approach to buffer the volume variation and enhance the electronic conductivity.[12,13] For example, the capacity of SnS_2 nanosheets with N-doped graphene (SnS_2/NGS) reaches 453 mA h g^{-1} at 0.1 A g^{-1}.[14] The ultrasmall SnS_2 nanoplate restacked on graphene with a three-dimensional (3D) network exhibits a discharge capacity of 650 mA h g^{-1} at 0.2 A g^{-1}.[15] The reversible capacity of SnS_2 nanosheet arrays is up to 631 mA h g^{-1} at 0.05 A g^{-1}.[16] Therefore, the structural stability and synergetic effects between SnS_2 and graphene lead to significantly improved sodium storage properties.

Metal compounds (like Cu, Fe, Ni, and Co-based) can also serve as a type of anode material for SIBs due to their conversion/recombination mechanism.[17–19] It is reported that introducing metallic Fe or Co cations can not only improve catalytic activity but also endow the compounds with a flexible structure to withstand the severe volume change of Sn and increase conductivity, resulting in improved initial coulombic efficiency (ICE) and cycling stability.[19–21] The specific capacity of Co-doped FeS_2 nanospheres is stabilized at 220 mA h g^{-1} after 5000 cycles and 172 mA h g^{-1} even at 20 A g^{-1} and still maintains a layered structure in the following cycles.[22] Therefore, the construction of Co-doped SnS_2 nanosheets grown on flexible carbon cloth (CC) will combine the virtues of different strategies and is expected as a novel approach for further enhancing the electrochemical properties of Sn-based anode materials.

According to our previous paper,[23] the SnS_2/CC anode reveals a specific capacity of 1039.9 mA h g^{-1} with a lower ICE of 32.8% at 0.2 A g^{-1}. To further improve the reversible

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Hierarchical nanosheet-assembled copper sulfide microspheres as the cathode materials for rechargeable magnesium batteries

Jiaqin Huang, Youqi Zhu*, Changliang Du, Zhanli Han, Xiuyun Yao, Xinyu Yang, Yuehua Cao, Yuexing Zhang, Xilan Ma, Chuanbao Cao*

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ABSTRACT

Rechargeable magnesium battery is an inexpensive, high-safety energy storage technology suitable for large-scale applications. However, its development is still hindered by lacking high-performance cathode materials. Herein, we present a simple one-step template-free hydrothermal method to synthesize hierarchical CuS microspheres self-assembled from nanosheets as the cathode materials for rechargeable magnesium battery. Owing to the special structure configuration, the as-synthesized CuS microspheres can exhibit a high specific capacity of 252 mAh g^{-1} at 100 mA g^{-1}, and a reversible specific capacity of 171.2 mAh g^{-1} at 500 mA g^{-1}. Additionally, the CuS microspheres also show good rate capability with 91.7 mAh g^{-1} specific capacity at high current density of 1000 mA g^{-1} and a long-term cycling stability over 500 cycles. These electrochemical results indicate that the fabrication of the CuS microspheres with hierarchical structure can provide an efficient route to develop high-performance copper sulfide cathode materials for emerging rechargeable magnesium batteries.

1. Introduction

In the past few decades, the huge consumption of traditional fossil fuels has brought about a series of global energy and environmental issues. At present, in order to make better use of renewable energy, it is an urgent need for efficient and sustainable energy storage systems. As an energy storage device that is expected to replace lithium-ion batteries, rechargeable magnesium batteries (rMBs) have a high theoretical specific capacity (2205 mAh g^{-1}) and volume capacity (3833 mAh cm^{-3}), and low reduction potential (2.37 V vs. SHE), abundant reserves and the dendritic-free nature of the magnesium anode [1–6]. Despite these advantages, rechargeable magnesium batteries are still subject to some challenges. For example, divalent Mg^{2+} ions have a high charge density, which makes Mg^{2+} diffusion very slow. In addition, there are relatively few active sites suitable for Mg^{2+} insertion in the matrix lattice. These shortcomings make the cathode materials suitable for rechargeable magnesium batteries very limited. At present, more and more alternative cathode materials have been proposed, including transition metal oxides such as TiO_2 [7,8], MnO_2 [9,10,11], V_2O_5 [12,13,14], and $VOPO_4$ [15,16], transition metal sulfides such as TiS_2, Ti_2S_4, CuS, and VS_4 [17–26], transition metal selenides such as $TiSe_2$, WSe_2, and CuSe [27–30], polyanionic compounds MgMSiO4 (M = Fe, Mn, Co) [31,32], Among these materials, most electrode materials cannot simultaneously exhibit good cycle stability or high specific capacity. Copper sulfide has become one of the most attractive cathode materials due to its low cost, high natural abundance, and large theoretical capacity (560 mAh g^{-1}) [33–37]. The combination of the cathode and metallic magnesium anode has the advantages of high energy storage and large-scale application.

Recent studies have shown that CuS not only has good conductivity and sufficient Mg^{2+} insertion voids, but also the weak interaction of Mg-S bonds, which can promote the magnesium migration and accelerate the electrochemical reaction kinetics. In 2020, Rashadet al. used fast magnesiation kinetics to investigate the development of electrolytes and cathode materials for magnesium ion batteries [38,39]. In addition, Rashad et al. also prepared nanocomposites by coating reduced graphene oxide on the surface of oxides to improve conductivity and optimize performance as a highly efficient cathode material for magnesium ion batteries [40]. The various structured CuS materials are used in magnesium batteries such as one-dimensional rods and tubes [24,41], two-dimensional sheets [42,43], and three-dimensional flowers and balls [44,45], which show that the electrochemical properties of CuS materials are highly depended on their morphology and

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Microwave-induced phase engineering of copper sulfide nanosheets for rechargeable magnesium batteries

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ABSTRACT

Phase controlling in transition metal dichalcogenides has been considered as a powerful route to regulate their chemical and electronic property for energy-related application yet is still subject to limited efficient fabrication method. We herein report a microwave-assisted strategy to synthesize Cu_xS nanosheets with tunable phases as high-performance cathode materials for rechargeable magnesium batteries. By precisely controlling the microwave irradiation time, the ultrathin two-dimensional Cu_xS nanosheets with graphene-like morphologies can be selectively prepared. The electrochemical measurements show that the specific capacities of different Cu_xS nanosheets strongly depend on their crystallographic structure and comply with a decreasing tendency of $Cu_{1.7}S > CuS > Cu_{1.9}S$. The multiphase $Cu_{1.7}S$ nanosheets delivers a capacity of 153.0 mAh g^{-1} at 300 mA g^{-1}, significantly higher than that 100.8 and 84.8 mAh g^{-1} of CuS and $Cu_{1.9}S$ counterparts. Moreover, $Cu_{1.7}S$ nanosheets display an excellent rate capability at various high current densities. Our work found that tuning the phase composition of Cu_xS could improve its electrochemical performances for rechargeable magnesium batteries. In addition, we offer a facile strategy to fabricate multiphase two-dimensional metal sulfide materials with great potential applications for energy devices.

1. Introduction

Two-dimensional (2D) transition metal dichalcogenides (TMDs) have great potential applications in electronic, optoelectronic, and energy conversion devices owing to their distinctive chemical and physical properties [1]. Hence, they have received increasing attention recently. In addition to composition, morphology, architecture, facet, size and dimensionality, crystalline phase of TMDs has arisen as an important structural parameter that determines the properties and functionalities [2]. Normally, various TMDs exhibit multiple phases with distinct properties. For example, Tashiro et al. compared two kinds of nanocrystalline cubic digenite copper sulfide (c-$Cu_{2-x}S$) and hexagonal chalcocite copper sulfide (h-$Cu_{2-x}S$) as cathode materials for rechargeable magnesium batteries (rMBs) [3]. They revealed that the rechargeable performance was only demonstrated with the c-$Cu_{2-x}S$ cathode in rMBs. Similar phenomena have been found in some transition metal oxides, such as MnO_2 [4,5] and TiO_{2-x} [6]. Moreover, the packing structures of organic cathode materials were also studied, for instance, π-conjugated polyimide-based organic cathodes [7]. Therefore, these materials with tunable phases synthesized by appropriate methods would provide a useful pathway to adjust their chemical properties, which has become an important topic in 2D material research.

Compared with many other TMDs, such as Mo_6S_8 [8,9], MoS_2 [10], Ti_2S_4 [11], NiS_x [12], VS_4 [13,14], VS_2 [15,16], α-Ag_2S [17], CoS [18,19] and CuSe [20], copper sulfides (Cu_xS, $xx = 1–2$) can form a series of nonstoichiometric compounds, including CuS [12], Cu_7S_4 [21], Cu_9S_5 [22] and Cu_2S [23] with crystal structures varying from orthogonal to hexagonal. To date, Cu_xS nanomaterials, such as nanosheets [23,24], nanoparticles [25,26], nanoplatelets [27], nanowires [28], nanospheres [29] and so on, have been fabricated by many different synthesis methods. However, it is still a challenge to control the phase of Cu_xS while keeping its morphology unchanged. CuS is a very promising cathode material for rMBs because of its high theoretical capacity (560 mAh g^{-1}), environmental friendliness and low cost [30]. However, the low solid-state Mg^{2+} ions transport kinetics in copper sulfides remains a major obstacle to its practical application. Hence, new strategies are urgently demanded to effectively design Cu_xS cathode mate-

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Tuning Surface Electronic Structure of Two-Dimensional Cobalt-Based Hydroxide Nanosheets for Highly Efficient Water Oxidation

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Highly exposing active sites and well tuning their electronic configuration are great challenges toward highly efficient oxygen evolution reaction (OER) catalysts. Herein, we demonstrate an in situ surface modification strategy for α and β-Co(OH)$_2$ nanosheets to boost their OER activities via a simple substitution of their surface hydroxyl functional groups by carboxylate or acetic anhydridate ones, respectively. This in situ surface modification can increase the areal densities of active sites and reduce the OER energy barriers while maintaining initial structure and morphology. Experimental results show that the modified catalysts can present much larger electrochemical active surface area (ECSA) and lower OER onset overpotential in comparison with the fresh ones. In case of carboxylate-modified α-Co(OH)$_2$ nanosheets, the onset overpotential has decreased from 266 to 233 mV and the required overpotential at 10 mA cm^{-2} has decreased from 309 to 288 mV on glassy carbon electrode. Density of states (DOS) calculations reveal an optimized adsorption energy of reaction intermediates. Remarkably, tuning surface electronic structure of catalyst by appropriately choosing highly electronegative functional groups can be considered as an efficient approach to enhance its OER activity.

Introduction

The electrochemical water splitting stands for a promising energy conversion and storage technology, which includes two half-reactions: hydrogen evolution reaction (HER) and oxygen evolution reaction (OER).[1] Their overall efficiency is particularly hampered by the sluggish OER kinetics with four electron transfer fairly to that of HER.[2] Even with the benchmarking RuO_2 and IrO_2 OER electrocatalysts, a considerably large overpotential is required and their scarcity further discourages their widespread adoption. Therefore, earth abundant transition metal (Mn, Fe, Co, and Ni) based hydroxides, oxides, carbides, nitrides, and sulfides are widely reported as low-cost and efficient OER electrocatalysts.[3] Particularly, Co-based layered double hydroxides (LDHs) have shown considerable OER activity due to their rich surface active sites and well-suited electronic configuration.[4] Additionally, the unique ultrathin two-dimension (2D) nanostructure can offer large surface area, short charge/mass diffusion paths, and abundant active sites.[5]

Although many efficient electrocatalysts are constantly being discovered, their optimization and mechanism studies have never stopped. Generally, tuning electronic structure of catalyst has proven to be an effective way to further enhance the OER performance through inducing oxygen and/or metal vacancies.[6,7] To decrease the free energy absorption of the OER intermediates (OH*, O*, and OOH*) and facilitate final product desorption is achievable for improving the overall OER performances.[8] Yanyong Wang *et al.* reported that the NiFe LDHs-V_{Fe} and NiFe LDHs-V_{Ni} electrocatalysts with rich iron or nickel vacancies can show excellent OER activity, which is attributed to efficiently tuning surface electronic structure and increasing the adsorbing capacity of OER intermediates.[6] Yunmin Zhu *et al.* exhibited that controlling oxygen vacancies in $PrBa_{0.5}Sr_{0.5}Co_{1.5}Fe_{0.5}O_{5+\delta}$ (PBSCF) can significantly improve in OER performance. In addition, cationic metal doping[9] and supported nanomaterials[10] have also been widely recognized to tune electronic structure, resulting in a synergistic effect from metal ions and metal-support interactions. Moreover, the catalyst surface state during OER is still a non-negligible factor in catalyst design process. Especially, avoiding catalyst surface poisoning caused the strong Vander Waals interactions between surfactant/solvent molecules and active sites, and surface wettability is considered to be an excellent solution for enhancing the exposed active site.[11] Therefore, it is an important goal to design catalyst with high exposure active sites and tune their electronic structures in an efficient manner for boosting their OER activity.

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发文日：

2021 年 03 月 24 日

申请号或专利号：**202110310273.6**　　发文序号：**2021032400959740**

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申请人：北京理工大学
发明创造名称：一种镁二次电池正极材料亚稳相 Cu 纳米管的制备方法

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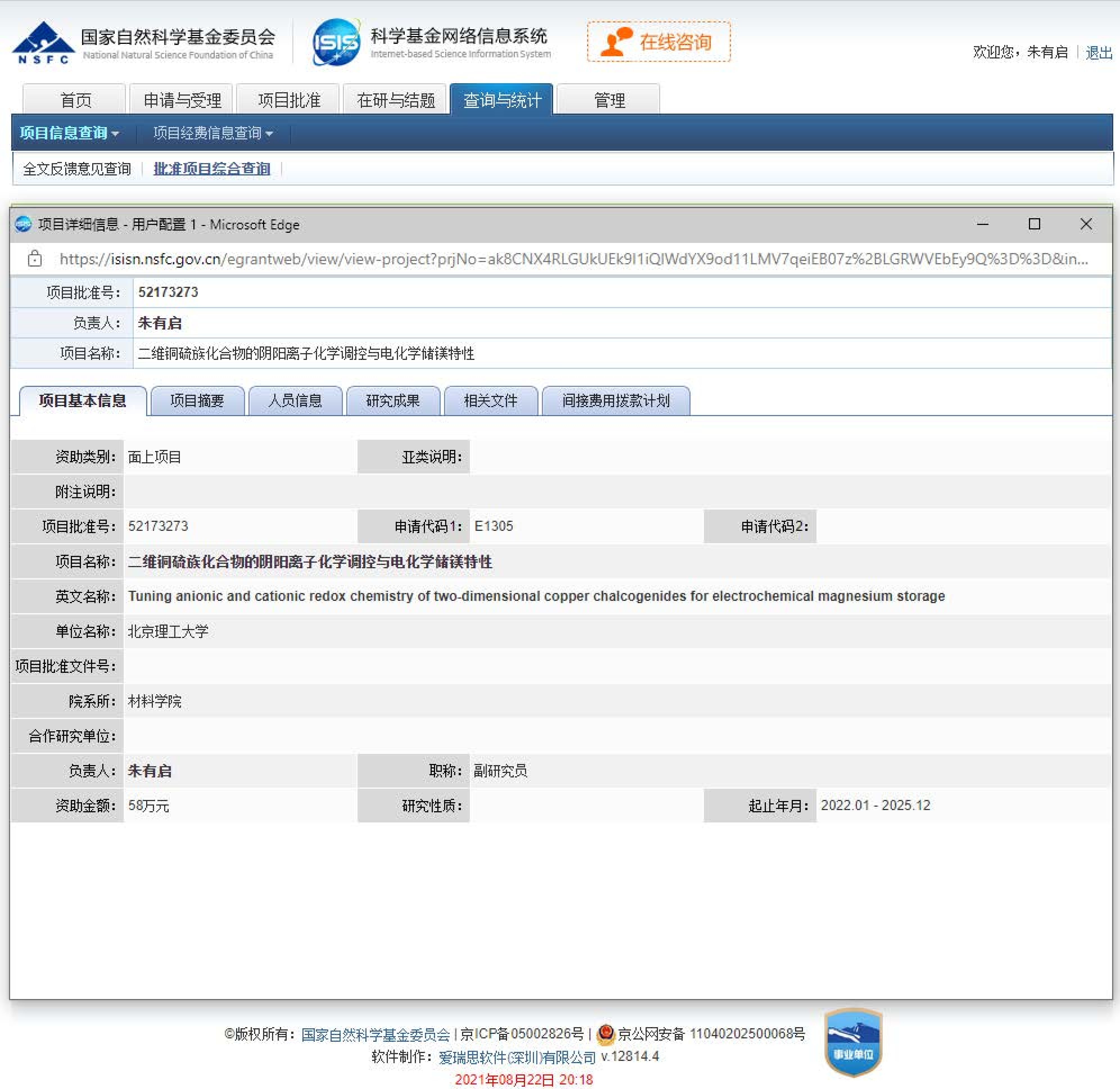

项目批准号：	52173273
负责人：	**朱有启**
项目名称：	二维铜硫族化合物的阴阳离子化学调控与电化学储镁特性

资助类别：	面上项目	亚类说明：			
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项目批准号：	52173273	申请代码1：	E1305	申请代码2：	
项目名称：	**二维铜硫族化合物的阴阳离子化学调控与电化学储镁特性**				
英文名称：	Tuning anionic and cationic redox chemistry of two-dimensional copper chalcogenides for electrochemical magnesium storage				
单位名称：	北京理工大学				
项目批准文件号：					
院系所：	材料学院				
合作研究单位：					
负责人：	**朱有启**	职称：	副研究员		
资助金额：	58万元	研究性质：		起止年月：	2022.01 - 2025.12

2021年08月22日 20:18

北京理工大学本科学生成绩单

开课学期：2019-2020-1	开课学院：材料学院
课程号：100091215	课程名称：半导体材料物理
成绩录入老师：朱有启	选课课号：(2019-2020-1)-100091215-6120180174-01
学时/学分：48/3.0	考试方式：正常　成绩评定方式：分数方式

序号	学号	姓名	行政班	录入总成绩	档案成绩	备注
1	1120162072	贾毅飞	09111701	[redacted]	[redacted]	缺考
2	1120170253	白志军	09111701	[redacted]	[redacted]	
3	1120170299	马雪花	09111701	[redacted]	[redacted]	
4	1120170388	徐超林	09111701	[redacted]	[redacted]	
5	1120170392	韦顺胜	09111701	[redacted]	[redacted]	
6	1120170395	刘晓东	09111701	[redacted]	[redacted]	
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10	1120171830	黄晓媛	09111701	[redacted]	[redacted]	
11	1120171853	管浩良	09111701	[redacted]	[redacted]	
12	1120172341	徐泰来	30091701	[redacted]	[redacted]	
13	1120172444	李昀玭	09111701	[redacted]	[redacted]	
14	1120172446	柴晓帅	09111701	[redacted]	[redacted]	
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17	1120172455	邓亦凡	09111701	[redacted]	[redacted]	
18	1120172458	孙泽文	09111701	[redacted]	[redacted]	
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22	1120173768	余羿	09111701	[redacted]	[redacted]	

期末成绩统计

百分制	五级记分制	二级记分制
90分以上 5人/23.8%	优秀	合格
80-89分 11人/52.4%	良好	不合格
70-79分 0人/0.0%	中等	
60-69分 5人/23.8%	及格	
不及格 0人/0.0%	不及格	

最高分 97　最低分 62　平均分 82.42

考试/查成绩统计

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80-89分 11人/52.38%	良好	不合格
70-79分 0人/0.00%	中等	
60-69分 5人/23.8%	及格	
不及格 0人/0.0%	不及格	
最高分 97　　最低分 62　　平均分 82.57		

考试简况

缺考人数	1	实到人数	21	缓考人数	0

任课教师（签字）：朱郁　　　　盖章：

考试/查日期：2020年1月13日

注：学生成绩录入完毕后，按规定格式打印一式三份正式成绩单，由任课教师签字确认后交学院教学办公室；开课单位将该成绩单加盖单位公章后一份留存、一份交教务处、一份用于试卷装订。原则上，任课教师也应保留一份成绩单存档。

教师课程表

2020-2021学年 2学期　　教师：朱有启(6120180174)

上课时间暂未确定的课程：	
调课信息：	

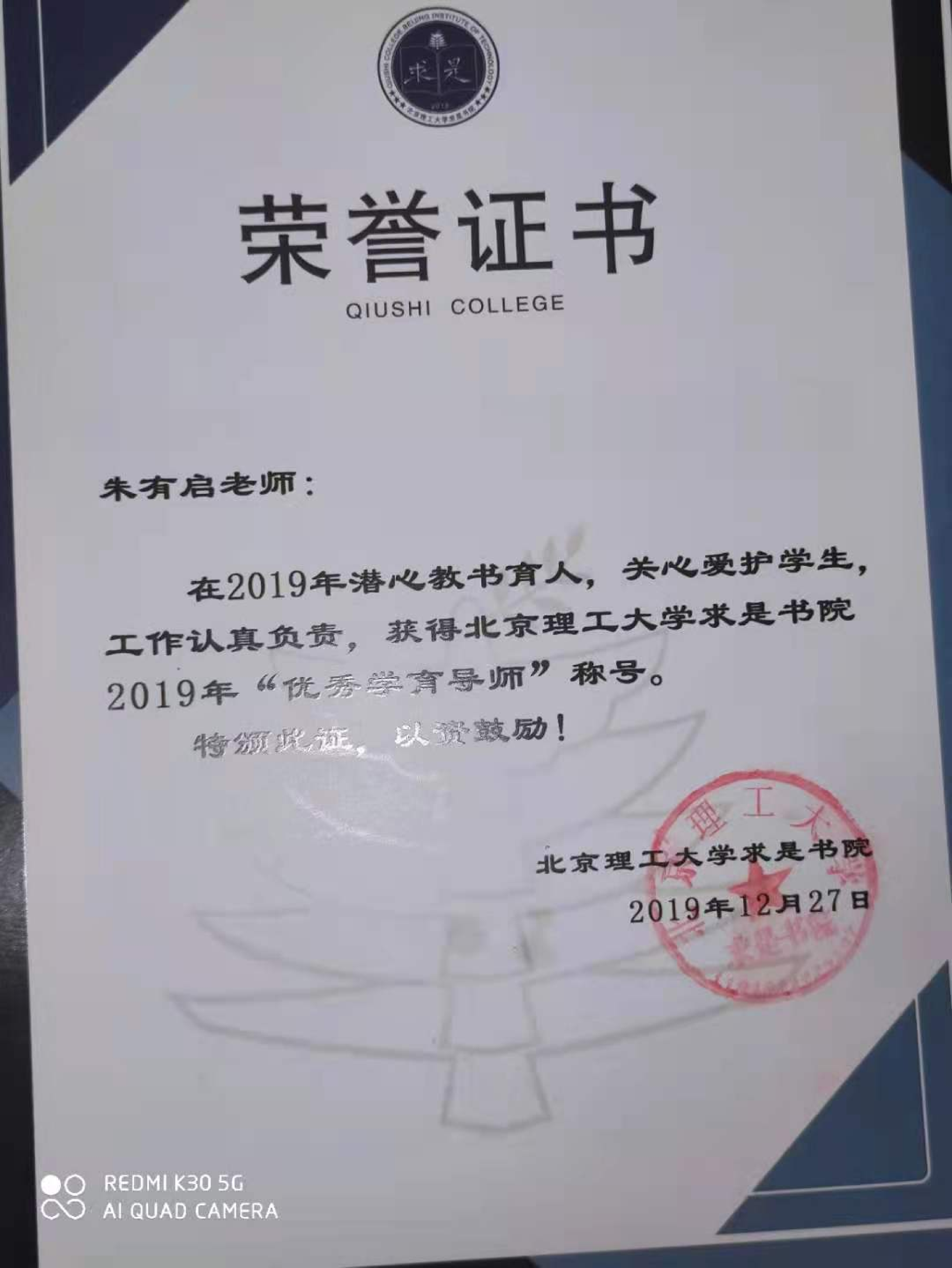
节次/星期	星期一	星期二	星期三	星期四	星期五	星期六	星期日
第1节-第2节							
第3节-第5节	（研）0900026-薄膜技术 [] 0 9-14周,星期1,第3节-第4节,研楼304 薄膜技术01, （研）0900026-薄膜技术 [] 0 9-13周,星期1,第5节-第5节,研楼304 薄膜技术01						
第6节-第7节							
第8节-第10节			（研）0900026-薄膜技术 [] 0 9-13周,星期3,第8节-第10节,研楼304 薄膜技术01				
第11节-第13节							

教师课程表

2020-2021学年 1学期　　教师：朱有启(6120180174)

上课时间暂未确定的课程:	
调课信息:	

节次/星期	星期一	星期二	星期三	星期四	星期五	星期六	星期日
第1节-第2节							
第3节-第5节				（本）100091219-新型无机材料及应用[211001101]22 7-8周,星期4,第3节-第4节,3号楼437 09111701(22)			
第6节-第7节	（本）100091219-新型无机材料及应用[211001101]22 7-8周,星期1,第6节-第7节,3号楼437 09111701(22)						
第8节-第10节							
第11节-第13节							



荣誉证书

QIUSHI COLLEGE

朱有启老师：

在2019年潜心教书育人，关心爱护学生，工作认真负责，获得北京理工大学求是书院2019年“优秀学育导师”称号。

特颁此证，以资鼓励！

北京理工大学求是书院
2019年12月27日