Applications and Challenges of 2D Materials in Lithium Metal Batteries

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Abstract

Owing to the high theoretical specific capacity and low electrochemical potential, lithium (Li) metal is considered as the most promising anode material for next-generation batteries. However, the commercial application of lithium metal batteries (LMBs) is restricted by Li dendritic growth and infinite volume change. Generally, introducing lithiophilic sites and constructing artificial solid-electrolyte interphase (SEI) layer are regarded as effective ways to induce uniform deposition of Li and inhibit growth of Li dendrites. 2D materials, due to their unique planar structure, high specific surface area, high mechanical strength and rich surface chemistry, are expected to achieve high performance LMBs with high stability and safety. Herein, the current progress of 2D materials for LMBs is summarized, focusing on constructing lithiophilic sites and artificial solid-electrolyte interphase (SEI) layer. Perspectives of future directions for LMBs are discussed. With the continuous research of 2D materials in LMBs, it is predictable that 2D materials will have great application prospects and make a difference in high-energy-density LMBs.

Key words: 2D materials; Li metal battery; Lithiophilic sites; Artificial SEI

1   Introduction

The rapid developments of mobile devices and electric vehicles have put forward an infinite demand for rechargeable batteries with high specific energy density. Lithium (Li) metal, considered as the "Holy Grail" anode, possesses an extra-high theoretical specific capacity (3860 mAh g^{-1}) and the ultra-low electrochemical potential (−3.04 V versus the standard hydrogen electrode)[1,2]. However, the commercial use of Li metal batteries (LMBs) still has a long way due to some tough issues[3,4]. The heterogeneous Li deposition behavior will cause the growth of Li dendrite, resulting in the formation of dead Li and low Coulombic efficiency[5]. Once the Li dendrite punctures the separator, a short circuit will occur in the LMBs, causing fire or even explosion[6]. Besides, the high reactivity of Li metal will result in continuous side reactions between Li metal and electrolyte with forming unstable solid electrolyte interphase (SEI) layers[7,8]. And owing to the hostless nature of Li metal anode, the volume change is virtually infinite during Li deposition process, which make it extremely unstable during cycles.

To solve these problems, several strategies have been explored to improve the cycle stability of LMBs. It is reported that Li metal will tend to nucleate at the lithiophilic sites due to strong adsorption energy[9,10]. By introducing lithiophilic sites on Li host, the Li nucleation behavior can be regulated, and Li dendrite growth can be inhibited to some extent. Besides, constructing a stable artificial SEI layer is also an important way to avoid the reaction between Li metal and electrolyte, thus improving cycle stability of LMBs[11].

Thanks to the unique chemical, physical, and mechanical properties, 2D materials, with sheet-like structure and atomic thickness, provide a great opportunity for the research and development of clean energy devices to meet the challenges of global energy demand[12–14]. In the field of LMBs, 2D materials not only exhibit abundant lithiophilic sites, but also can participate in the construction of artificial SEI layers, which are of great help to improve the performance of LMBs. Herein, we briefly summarize our progress about 2D materials as lithiophilic sites or as artificial SEI layer. Some perspectives for the future development of 2D materials in LMBs are also given. We hope this summary will provide some new insights into this exciting area.

2   Two-dimensional materials in lithium metal anode

2.1   2D materials with lithiophilic sites

The lithiophilicity refers to the affinity to Li species of Li hosts. Lithiophilic sites can effectively induce lower nucleation barriers as well as the more homogeneous Li nucleation, leading to a dendrite-free Li plating behavior. Thus, the lithiophilicity of electrode can play an important role in the construction of high performance LMBs. Up to now, tremendous progress has been achieved in designing electrodes with lithiophilic sites, which are composed of carbons materials[15], alloys[16], and polymers[17]. For example, it is found that re-

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duced graphene oxide (rGO) exhibits high lithiophilicity sites[18], which can regulate the Li nucleation behavior and inhibit Li dendrite growth. However, the limited amount of such intrinsic lithiophilic sites and relative low ability to adsorb Li make it difficult to obtain excellent performance LMBs. Luckily, it is found that hetero atom doping in graphene, such as N-doped graphene and B-doped graphene[19–21], can effectively increase the number of lithiophilic sites and enhance the binding energy to Li atoms. However, the nitrogen-doped graphene may react with lithium to form lithium nitride during the long-term cycling, resulting in the decrease of lithiophilicity sites and capacity loss. To solve this problem, Zhai et al. introduce single-atom (SA) metals doping on nitrogen-

doped graphene (SAM-NG) to form M-N$_x$-C sites. These lithiophilic sites can not only increase the Li adsorption energy around the metal atomic sites but prevent the structural damage during the long-term cycling, thus uniform nucleation and dendrite-free deposition can be achieved (Fig. 1a)[22]. As a result, the single-atom Ni doping on nitrogen-doped graphene (SANi-NG) electrode exhibits a high average Coulombic efficiency of 98.45% over 250 cycles with a capacity of 1.0 mAh cm^{-2} at current density of 0.5 mA cm^{-2}, and a stable Li plating/stripping performance even at a high current density of 4.0 mA cm^{-2}. On this basis, Yang et al. further proposed the concept of reversible lithiophilic sites, where the binding energy to Li atoms should be within a certain threshold
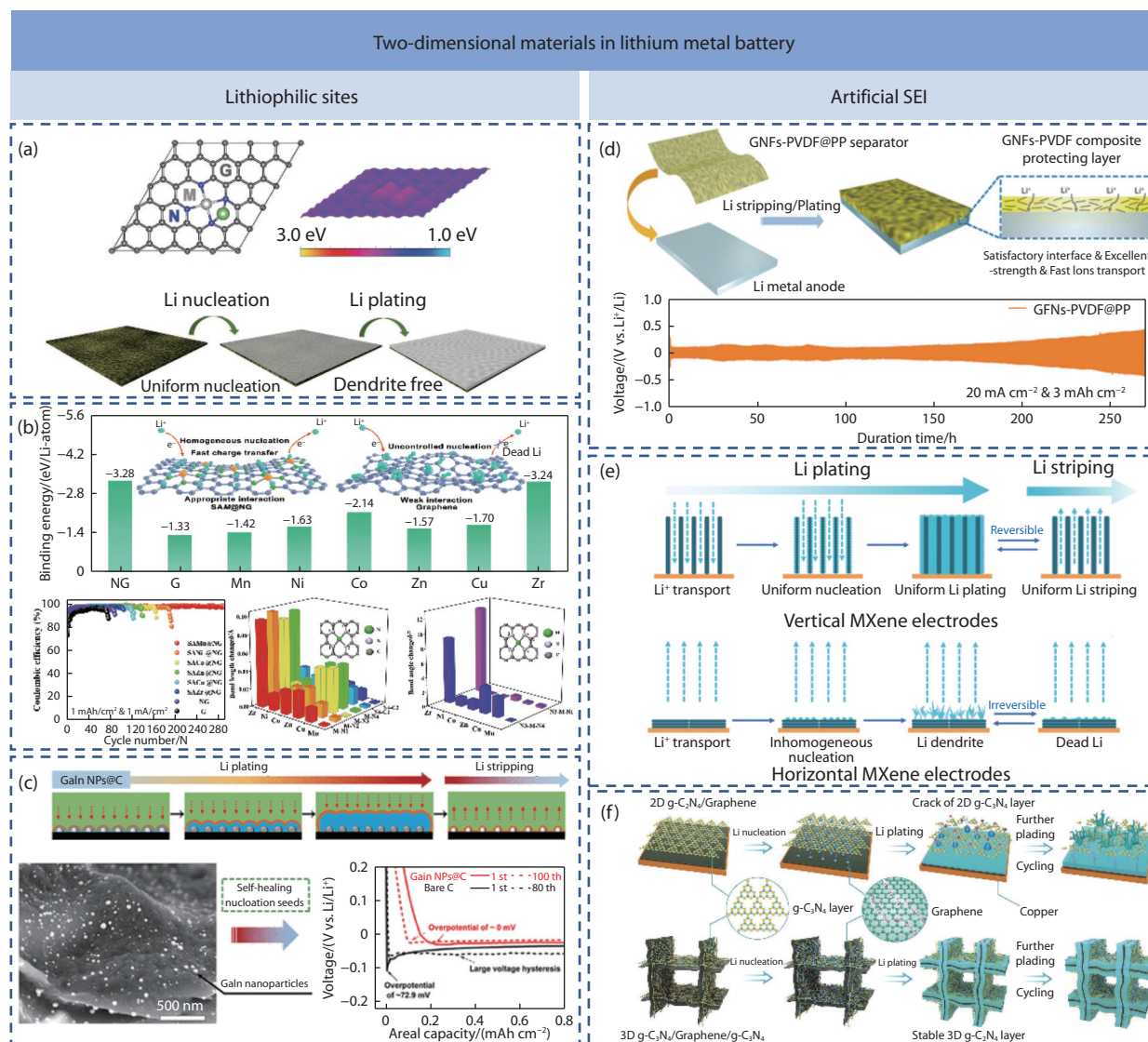

Fig. 1 2D materials in LMBs. (a) Li adsorption energy distribution mappings and corresponding schematic illustrations of Li nucleation and plating process on SA metal-NG electrode[22]. Copyright 2019, Wiley-VCH. (b) Binding energy of Li atoms on different substrates and coulombic efficiency of Li deposition on electrodes with a capacity of 1 mAh cm^{-2} at 1 mA cm^{-2}[23]. Copyright 2022, Wiley-VCH. (c) Schematic illustration and SEM image of uniform Li plating/stripping behavior seeded by liquid GaIn NPs and voltage-areal capacity curve corresponding to the nucleation process of bare C and GaIn NPs@C electrodes[24]. Copyright 2021, American Chemical Society. (d) Schematic illustrations of Li deposition and surface structure on Li metal anodes with GFNs-PVDF@PP separator and Electrochemical performances of symmetric Li|Li cells with a capacity 3 mAh cm^{-2} at a current density of 20 mA cm^{-2}[28]. Copyright 2020, American Chemical Society. (e) Schematic illustration of uniform Li plating/stripping behavior of vertical MXene electrodes and horizontal MXene electrodes[29]. Copyright 2022, Wiley-VCH. (f) Illustration of Li deposition in the van der Waals gap between graphene and g-C$_3$N$_4$[30]. Copyright 2021, Wiley-VCH.

range, *i.e.,* strong enough to inhibit Li dendrites growth and weak enough to avoid host structure collapse[23]. Theoretical calculations reveal that different SAM-NG shows different binding energy for Li adsorption. Despite SAZr-NG shows the biggest (−3.24 eV) binding energy in the SAM-NG systems, the electrochemical performance in SAZr-NG is not good enough from experiments. This result indicates that binding energy of Li on lithiophilic sites is not a positively correlated criterion to evaluate and understand the performance of LMBs. Benefitting from the little change of the chemical structures during Li plating/stripping, SAMn-NG exhibits the most reversible lithiophilic site with the longest cycle life (over 290 cycles) and highest average CE (99.0%) with a capacity of 1.0 mAh cm^{-2} at current density of 1.0 mA cm^{-2} (Fig. 1b).

In addition to regulating lithiophilic properties of 2D materials by single atom doping, loading lipophilic materials on 2D materials is also an effective way to introduce lithiophilic sites. Zhai et al. report that the GaIn nanoparticles uniformly decorated on surface of porous carbon layers (GaIn NPs@C) can protect Li metal from dendrite and dead Li formation[24]. The GaIn NPs will react with Li to form the Ga−In−Li alloy with Li plating, which can decrease the Li nucleation barrier to induce the uniform Li nucleation and deposition with long-term cycling stability (Fig. 1c). More importantly, GaIn NPs can be self-healed after Li stripping due to the nature of liquid metal. Benefitting from these advantages, the GaIn NPs@C electrode exhibits an ultralow nucleation overpotential (nearly 0 mV) and a greatly improved cycling stability for more than 400 cycles with a high average coulombic efficiency of 99.03% at 1.0 mA cm^{-2} with a cycling capacity of 1.0 mAh cm^{-2}.

2.2 2D Materials as Artificial SEI

Generally, SEI layer comes from the reaction between the Li metal and the organic electrolyte during the initial charge–discharge process. An ideal SEI layer should possess the high ionic conductivity, rational thickness, high mechanical strength, and electro-chemical stability during battery charge/discharge process. However, the natural SEI layer has uneven distribution and low mechanical strength. These shortcomings make it easy to be broken and constantly be re-generated during charge/discharge cycles, resulting in dendrite formation and continuous consumption of electrolyte[25–27]. One effective method is to build protective films as artificial SEI to avoid continuous side reactions between lithium and electrolyte.

Taking the ultrathin planar structure, high mechanical strength and rich surface chemistry into account, 2D materials have been proved to be appropriate to work as artificial SEI layer. For example, 2D materials can react with Li during the activate process to form an in-situ protecting layer upon Li metal anode. Xiao et al. report a graphite fluoride nanosheets and poly(vinylidene difluoride) modified separator (GFNs-PVDF@PP) to in-situ construct a protective layer for Li metal anodes[28]. In addition, 2D nanomaterials could further improve the mechanical strength of the polymer based artificial SEI layer because of grain refinement effect. Due to the much-improved mechanical properties of elastic modulus and toughness, this GFNs-PVDF protective layer is competent to effectively curb the growth of Li dendrites and maintain self-integrity under stress fluctuations. The GFNs can react with Li metal to form graphite nanosheets (GNs) and LiF protect layer, which can not only provide fast transport channels for Li ions but also protect the Li metal anode from continuous reaction with electrolytes (Fig. 1d). As a result, the cells with GFNs-PVDF@PP separator obtain a stable Li plating/stripping of over 250 h at a high current density of 20 mA cm^{-2} and a large specific capacity of 3 mAh cm^{-2}.

Besides, the rich functional groups on the surface of 2D materials can also be applied to react with Li to construct SEI layers. Chen et al. report 3D vertical Ti$_3$C$_2$T$_x$ arrays (v-Ti$_3$C$_2$T$_x$) by a facile ice template assisted blade coating method[29]. The abundant O and F containing groups on the surface of Ti$_3$C$_2$T$_x$ can react with Li ions to in-situ form uniform SEI layers consisting of Li$_2$O and LiF. Compared to horizontal structure (Fig. 1e), the 3D structure can effectively homogenize the Li ions flux and alleviate the volume expansion during lithium deposition, thus the vertical Ti$_3$C$_2$T$_x$ electrode with uniform SEI layer can realize dendrite-free lithium deposition and maintain the structure stable during the Li plating/striping cycles. Consequently, the vertically aligned Ti$_3$C$_2$T$_x$ electrodes can achieve a high average coulombic efficiency of 98.8% for more than 450 cycles at a fixed areal capacity of 1.0 mAh cm^{-2} with a current density of 1.0 mA cm^{-2}.

Furthermore, some materials that do not participate in the electrode reaction can be directly used as artificial SEI layer to protect Li metal anode. Zhai et al. put forward a sandwiched heterostructure constructed by g-C$_3$N$_4$/graphene/g-C$_3$N$_4$ layers[30]. The chemically stable g-C$_3$N$_4$ layer can play an important role as 3D artificial SEI layer, which not only provide abundant N species for Li nucleation but also induce Li deposition in the van der Waals gap between graphene and g-C$_3$N$_4$. And the 3D graphene skeleton can reduce the local current density and moderate volume change during Li plating/stripping process (Fig. 1f). As a result, the 3D g-C$_3$N$_4$/G/g-C$_3$N$_4$ electrode enables high average CE of 98.7% at a high capacity of 5.0 mAh cm^{-2} at a current density of 2.0 mA cm^{-2} and a long-term cycling behavior (more than 500 cycles) with a high Coulombic efficiency (average 99.1%) at a capacity of 1.0 mAh cm^{-2}.

3 Discussion and perspective

Despite Li metal exhibits extremely high theoretical specific capacity and the lowest electrochemical potential, there are still many problems demanding prompt solution for its commercial application. Benefiting from its plane structure, high specific surface area and rich surface chemistry, the introduction of 2D materials can contribute to the realization of efficient and sustainable Li metal anode. On the one hand, 2D materials with lithiophilic sites can regulate the Li nucleation behavior and further induce uniform Li deposition. On the other hand, 2D materials are capable to work as artificial SEI layers, which can protect the Li metal anode from continuous reaction with electrolytes and inhibit Li dendrite growth.

However, the research of Li metal batteries based on 2D materials is just the tip of the iceberg. Up to now, most of the work has focused on 2D carbon materials, which means the remaining 2D materials are urgently awaited to explore their performance by experimental verification and computational

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simulation. Besides, it is of great significance to develop all-solid state Li metal battery to solve its safety problems. And 2D materials with high mechanical strength and high ionic conductivity can be appropriate candidates to modify the interface between Li metal and solid electrolyte. On the other hand, electrolyte modification is considered to be one of the most fundamental solutions to improve the safety of LMBs by adding 2D materials as effective additives. Moreover, inspired by the intercalation mechanism of 2D materials in the field of Li-ion batteries, it is possible for Li metal deposition in van der Waals gap by intercalating lithiophilic sites between layers of 2D materials. While in this region, there are few reports till now.

In terms of practical application, there are still some concerns limiting the development of LMBs. A sharp problem is the high initial capacity loss caused by the formation of SEI layer on anode, leading to the consumption of Li ions and a low Coulombic efficiency in the initial cycle. It is considered that prelithiation technology is the key to solve this problem, which means providing additional reactive Li before the battery assembly to compensate the lost capacity. Therefore, it is of great practical significance to further explore low cost prelithiation materials and technologies for the development of LMBs.

Apart from this, the current thickness of Li foil cannot meet the requirements for Li metal anode (<50 μm). It is considered to obtain the Li metal anode with ultrathin thickness by electrochemical deposition, which works well in coin-cell. However, this method might not work under the situation of large-scale ultra-thin Li foil preparation. The possible reason is that the contact between the deposited Li metal and the anode material is not close enough due to the lack of external pressure. The behavior and mechanism of large-scale ultra-thin Li foil preparation by electrochemical deposition or other methods remain to be explored.

More attentions should be paid on the issues of long cycles performance under extreme conditions, such as less electrolyte, less Li or even anode-free conditions. However, most of the current research about LMBs is conducted by assembling coin cell instead of pouch cell, which do not meet above requirements. Therefore, the operating conditions and the needs of industrialization must be considered before designing and testing LMBs.

Acknowledgments

Conflict of interest

The authors declare no conflict of interest.

Author contributions

Qian Chen: Writing-Original Draft; Yongji Gong: Writing-Review & Editing; all authors had approved the final version.

REFERENCES

1. W. Xu, J. Wang, F. Ding, X. Chen, E. Nasybulin, Y. Zhang, J.-G. Zhang, *Energ. Envrion. Sci.*, 2014, 7, 513
2. D. Lin, Y. Liu, Y. Cui, *Nat. Nanotechnol.*, 2017, 12, 194
3. B. Liu, J.-G. Zhang, W. Xu, *Joule*, 2018, 2, 833
4. J. Xiao, Q. Li, Y. Bi, M. Cai, B. Dunn, T. Glossmann, J. Liu, T. Osaka, R. Sugiura, B. Wu, J. Yang, J.-G. Zhang, M. S. Whittingham, *Nat. Energy*, 2020, 5, 561
5. X.-B. Cheng, R. Zhang, C.-Z. Zhao, Q. Zhang, *Chem. Rev.*, 2017, 117, 10403
6. R. Xu, J.-F. Ding, X.-X. Ma, C. Yan, Y.-X. Yao, J.-Q. Huang, *Adv. Mater.*, 2021, 33, 2105962
7. T. Li, H. Liu, P. Shi, Q. Zhang, *Rare Metals*, 2018, 37, 449
8. C. Yan, R. Xu, Y. Xiao, J.-F. Ding, L. Xu, B.-Q. Li, J.-Q. Huang, *Adv. Funct. Mater.*, 2020, 30, 1909887
9. R. Zhang, X.-R. Chen, X. Chen, X.-B. Cheng, X.-Q. Zhang, C. Yan, Q. Zhang, *Angew. Chem. Int. Edit.*, 2017, 56, 7764
10. Y.-X. Zhan, P. Shi, X.-X. Ma, C.-B. Jin, Q.-K. Zhang, S.-J. Yang, B.-Q. Li, X.-Q. Zhang, J.-Q. Huang, *Adv. Energy. Mater.*, 2022, 12, 2103291
11. B. Liu, Y. Zhang, G. Pan, C. Ai, S. Deng, S. Liu, Q. Liu, X. Wang, X. Xia, J. Tu, *J. Mater. Chem. A*, 2019, 7, 21794
12. P. Zhai, L. Liu, X. Gu, T. Wang, Y. Gong, *Adv. Energy. Mater.*, 2020, 10, 2001257
13. C. Zhang, A. Wang, J. Zhang, X. Guan, W. Tang, J. Luo, *Adv. Energy. Mater.*, 2018, 8, 1802833
14. H. Que, H. Jiang, X. Wang, P. Zhai, L. Meng, P. Zhang, Y. Gong, *Acta Phys.-Chim. Sin.*, 2021, 37, 2010051
15. L. Chen, H. Chen, Z. Wang, X. Gong, X. Chen, M. Wang, S. Jiao, *Chem. Eng. J.*, 2019, 363, 270
16. S.-S. Chi, Q. Wang, B. Han, C. Luo, Y. Jiang, J. Wang, C. Wang, Y. Yu, Y. Deng, *Nano Lett.*, 2020, 20, 2724
17. C.-H. Chang, S.-H. Chung, A. Manthiram, *Adv. Sustain. Syst.*, 2017, 1, 1600034
18. D. Lin, Y. Liu, Z. Liang, H.-W. Lee, J. Sun, H. Wang, K. Yan, J. Xie, Y. Cui, *Nat. Nanotechnol.*, 2016, 11, 626
19. W. Liu, P. Zhai, S. Qin, J. Xiao, Y. Wei, W. Yang, S. Cui, Q. Chen, C. Jin, S. Yang, Y. Gong, *J. Energy. Chem.*, 2021, 56, 463
20. Y. Li, Y. Li, Y. Sun, B. Butz, K. Yan, A. L. Koh, J. Zhao, A. Pei, Y. Cui, *Nano Lett.*, 2017, 17, 5171
21. Q. Yang, M. Cui, J. Hu, F. Chu, Y. Zheng, J. Liu, C. Li, *ACS Nano*, 2020, 14, 1866
22. P. Zhai, T. Wang, W. Yang, S. Cui, P. Zhang, A. Nie, Q. Zhang, Y. Gong, *Adv. Energy Mater*, 2019, 9, 1804019
23. Z. Yang, Y. Dang, P. Zhai, Y. Wei, Q. Chen, J. Zuo, X. Gu, Y. Yao, X. Wang, F. Zhao, J. Wang, S. Yang, P. Tang, Y. Gong, *Adv. Energy Mater.*, 2022, 12, 2103368
24. P. Zhai, L. Liu, Y. Wei, J. Zuo, Z. Yang, Q. Chen, F. Zhao, X. Zhang, Y. Gong, *Nano Lett.*, 2021, 21, 7715
25. Y. Li, Y. Li, A. Pei, K. Yan, Y. Sun, C.-L. Wu, L.-M. Joubert, R. Chin, L. Koh Ai, Y. Yu, J. Perrino, B. Butz, S. Chu, Y. Cui, *Science*, 2017, 358, 506
26. R. L. Sacci, N. J. Dudney, K. L. More, L. R. Parent, I. Arslan, N. D. Browning, R. R. Unocic, *Chem. Commun.*, 2014, 50, 2104
27. Q. Wu, Y. Zheng, X. Guan, J. Xu, F. Cao, C. Li, *Adv. Funct. Mater.*, 2021, 31, 2101034
28. J. Xiao, P. Zhai, Y. Wei, X. Zhang, W. Yang, S. Cui, C. Jin, W. Liu, X. Wang, H. Jiang, Z. Luo, X. Zhang, Y. Gong, *Nano Lett.*, 2020, 20, 3911
29. Q. Chen, Y. Wei, X. Zhang, Z. Yang, F. Wang, W. Liu, J. Zuo, X. Gu, Y. Yao, X. Wang, F. Zhao, S. Yang, Y. Gong, *Adv. Energy Mater.*, 2022, 12, 2200072
30. P. Zhai, T. Wang, H. Jiang, J. Wan, Y. Wei, L. Wang, W. Liu, Q. Chen, W. Yang, Y. Cui, Y. Gong, *Adv. Mater.*, 2021, 33, 2006247

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