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Fully Solar-Powered Uninterrupted Overall Water-Splitting Systems

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Extensive research effort has recently been devoted to the development of self-driven electrocatalytic water-splitting systems to generate clean hydrogen chemical fuels. Currently, self-driven electrocatalytic water-splitting devices are powered by solar cells, which operate intermittently, or by aqueous batteries, which deliver stored electric power, leading to high operating costs and environmental pollution. Thus, a fully solar-powered uninterrupted overall water-splitting system is greatly desirable. Here, we successfully assembled the solar cells, stable output voltage of 1.75 V Ni-Zn batteries and high efficiency zinc-nickel-cobalt phosphide electrocatalysts together to create a 24-hour overall water-splitting system. Specifically, the silicon-based solar cells enable to charge aqueous Ni-Zn batteries for energy storage as well as provide sufficient energy for electrocatalysis throughout the day; in addition, the high-capacity Ni-Zn batteries offer a steady output voltage for overall water-splitting at night. Such an uninterrupted solar-to-hydrogen system opens up exciting opportunities for the development and application of renewable energy.

1. Introduction

The excessive use of fossil fuels has led to an increasing energy crisis and severe climate warming, thus directing tremendous attention to the development of renewable and green energy

technologies^[1-18]. Water splitting is a fast and cost-effective strategy for converting and storing intermittent solar and wind energy in the form of hydrogen and oxygen chemical fuels^[19-21]. Although significant progress has been made in the study of non-precious transition metal sulfides, phosphides and nitride electrocatalysts, self-driven electrocatalytic water-splitting devices are directly powered by solar cells or rechargeable batteries^[22-31]. The former method has great limitations due to the intermittent nature of sunlight, and the latter inevitably uses electricity derived from the power grid, leading to high costs and environmental pollution. Therefore, the design and development of fully solar-powered uninterrupted overall water-splitting systems for hydrogen generation are highly desirable yet greatly challenging.

Generally, dedicated catalysts show high catalytic activities for the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) for water splitting at a high driven voltage of 1.8-2.0 V, which is much higher than the minimal thermodynamic water-splitting potential of 1.23 V. Thus, high-voltage batteries can effectively drive overall water splitting. As a feasible energy supply, Ni-Zn batteries play a highly important role in electrocatalysis for overall water splitting due to their high output voltage of ~1.75 V and long-term safety^[32-36]. However, the main bottleneck in the development of Ni-Zn batteries for this purpose is low specific capacity due to the lack of a high-performance Ni-based cathode, making self-driven water-splitting devices difficult to achieve.

Herein, as a proof-of-concept demonstration, we successfully assembled solar cells incorporating Ni-Zn batteries with a stable output voltage of 1.75 V and high-efficiency electrocatalysts composed of zinc-nickel-cobalt phosphide nanowire arrays (ZNCP NWAs) to achieve 24-hour overall water splitting without interruptions or degradation. In particular, the solar

cells, as the sustainable energy input, charge the rechargeable Ni-Zn batteries for energy storage and provide a steady voltage for electrocatalysis throughout the day. More importantly, the ultrahigh-capacity Ni-Zn batteries can provide a steady output voltage for self-driven overall water electrocatalysis splitting at night. Thus, the present study offers a promising strategy for fabricating multifunctional devices that require only sunlight to run, representing an important step in the sustainable development of green and renewable energy management.

2. Results and discussion

Figure 1 illustrates a schematic of the fabrication of the fully solar-powered uninterrupted overall water-splitting system for both energy storage and conversion. The device features a commercial planar polycrystalline Si solar cell (PSSC), rechargeable Ni-Zn batteries and ZNCP NWAs/Ni foam (NF) electrocatalysts for the HER and OER, respectively. Specific details are presented in the experimental section. In principle, the PSSC can convert solar energy to electricity for charging the Ni-Zn batteries and provide a steady voltage for electrocatalysis during the day synchronously. Moreover, the high-capacity Ni-Zn batteries can provide a steady output voltage for overall water electrocatalysis splitting at night. Based on this systematic energy storage and conversion scheme, fully solar-powered uninterrupted overall water-splitting systems are obtained.

Three-dimensional (3D) well-aligned zinc-nickel-cobalt oxide (ZNCO) NWAs were directly grown on NF by the hydrothermal method and subsequent high-temperature calcination. Corresponding scanning electron microscopy (SEM) images obtained at various magnifications and energy-dispersive spectroscopy (EDS) mappings of ZNCO NWAs are shown in Figure S1 and S2. The EDS spectrum of the ZNCO NWAs presented in Figure S3 clearly illustrates that the cobalt atoms are partially replaced by both zinc and nickel atoms, proving the successful fabrication of Zn/Ni co-doped Co_3O_4 . It is clearly shown that ultrathin $\text{Ni}(\text{OH})_2$ nanosheets were uniformly

anchored onto the surfaces of ZNCO NWAs after the chemical bath deposition process (Figure 2a), forming hierarchical core-shell heterostructures, as further confirmed by TEM (Figure 2b and Figure S4). The ZNCO NWAs exhibit diffraction peaks centered at 18.7° , 30.9° , 36.5° , 44.5° , 59.0° , and 64.7° (Figure S5) and slightly shifted in comparison with the spinel Co_3O_4 (JCPDS card no. 74-2120), further indicating forming Zn/Ni co-doped Co_3O_4 . According to the XRD patterns in Figure S5, the core-shell heterostructures exhibit only the major diffraction peaks of both ZNCO and $\text{Ni}(\text{OH})_2$ without any extra peaks. The EDS mapping images in Figure S6 demonstrate the homogeneous elemental distribution of Zn, Ni, Co and O, confirming the ZNCO core/ $\text{Ni}(\text{OH})_2$ shell hierarchical structure. To further investigate the chemical compositions and valence states of the ZNCO@ $\text{Ni}(\text{OH})_2$ NWAs, X-ray photoelectron spectroscopy (XPS) was also performed (Figure S7). The electrochemical performance of the ZNCO@ $\text{Ni}(\text{OH})_2$ NWAs was measured in a 1 M KOH aqueous electrolyte. Figure 2c shows the discharge curves of the ZNCO@ $\text{Ni}(\text{OH})_2$ NWAs/NF electrode at different current densities between 2 and 12 mA/cm^2 . Remarkably, the ZNCO@ $\text{Ni}(\text{OH})_2$ NWAs achieve an excellent capacity of 16.9 mAh/cm^2 at a current density of 2 mA/cm^2 and maintain a capacity of 13.8 mAh/cm^2 as the current density increases to 12 mA/cm^2 . Compared with pristine Co_3O_4 and $\text{Ni}(\text{OH})_2$, Zn/Ni co-doped Co_3O_4 is an excellent secondary substrate for the growth of $\text{Ni}(\text{OH})_2$ (Figure S8). In addition, our work demonstrated that the specific capacitance of ZNCO@ $\text{Ni}(\text{OH})_2$ NWAs is much higher than that for the ZNCO NWAs and $\text{Ni}(\text{OH})_2$ nanosheet electrodes^[37]. To further verify the potential application of the ZNCO@ $\text{Ni}(\text{OH})_2$ NWAs/NF electrode for Ni-Zn batteries, an aqueous Ni-Zn battery was assembled with ZNCO@ $\text{Ni}(\text{OH})_2$ /NF as the cathode and a Zn plate as the anode, as depicted in Figure 2d. The

schematic fabrication process of the assembled Ni-Zn batteries is shown in Figure S9. The typical galvanostatic charge-discharge (GCD) curves of the Ni-Zn battery in Figure 2e exhibit high charge and discharge plateaus at different current densities ranging from 1 mA/cm² to 12 mA/cm². More importantly, a prominent areal capacity of 11.2 mAh/cm² is achieved for the as-assembled Ni-Zn battery, substantially outperforming most previously reported aqueous batteries^[33,38-40]. The areal energy and power densities of our Ni-Zn battery are depicted in Figure 2f. Encouragingly, our device delivered a remarkable energy density of 19.6 mWh/cm² at a current density of 2 mA/cm². The Nyquist plot of the electrochemical impedance is illustrated in Figure S10. A single Ni-Zn battery can be integrated in series to achieve higher operating voltages for practical applications (Figure S11).

Solar power is arguably the most abundant and renewable energy source. It is highly urgent to develop efficient energy conversion and storage technologies to exploit the intermittent nature of sunlight. Thus, constructing high-performance rechargeable battery-solar cell integrated devices is an extremely effective way to achieve continuous energy supply. Figure 3a presents a schematic illustration of the as-prepared Ni-Zn battery charged by a commercial planar PSSC. As shown in Figure 3b, the PSSC device exhibits an open-circuit voltage of 9.2 V and a short-circuit current of 11.2 mA under AM 1.5 illumination. It should be noted that the open-circuit voltage and short-circuit current of the PSSC device remained nearly unchanged under AM 1.5 illumination for 12 h (Figure 3c), indicating excellent stability. Figure 3d compares the charge curves of the Ni-Zn battery under different light intensities with the same illumination duration of 600 seconds. It can be clearly observed that the charging plateaus of the Ni-Zn battery rose as the light intensity increased.

As shown in Figure 3e, the as-prepared Ni-Zn battery could be charged to 1.95 V by PSSC in 168 minutes, and it could be galvanostatically discharged to 1.4 V with a current density of 2 mA/cm² in 272 minutes, demonstrating the practical application of our solar-charged Ni-Zn battery. Such a solar-charged Ni-Zn battery is expected to drive overall water splitting without interruption.

Excellent catalysts for overall water splitting must possess remarkable bifunctional HER and OER performance in alkaline solution. Herein, 3D self-supported ZNCP NWAs on NF were obtained via a one-step phosphidation treatment of ZNCO NWAs, as shown in Figure 4a and S12. Notably, the nanowire consisted of a number of nanoparticles (Figure 4b). EDS mapping and XPS were carried out to further analyse the elemental composition of the ZCNP NWAs, and the detailed results are shown in Figure 4e and S13, implying the presence of P. The HER and OER performances of ZNCP, ZNCO, and NF were measured by a three-electrode system in a 1.0 M KOH electrolyte. As depicted in Figure S14, the ZNCP NWAs/NF can achieve a low overpotential of 137 mV at a current density of 50 mA/cm², which is significantly lower than the values of ZNCO NWAs (390 mV) and NF (470 mV), suggesting that ZNCP NWAs/NF possesses remarkable HER activity. Furthermore, the typical OER linear sweep voltammetry curves shown in Figure S15 demonstrate that ZNCP NWAs/NF presented a higher current density than did ZNCO NWAs/NF and NF, verifying the catalyst's remarkable OER performance. Figure 4d shows the voltage difference (ΔV) between the HER and OER; a potential of 1.637 V is required to attain a current density of 50 mA/cm². Given the impressive bifunctional catalytic activities observed, the steady-state polarization curve for overall water splitting of ZNCP nanowires was measured (Figure 4e), presenting a current density of 20 mA/cm² with an external bias of 1.615 V, which is superior

to most previously reported results^[22, 26, 41-43]. In addition, electrocatalysts must possess high durability for practical applications. Figure 4f displays the potential-time curve of ZNCP nanowires, whose overpotential remained almost invariant for a long testing period of approximately 200 h at a steady-state current density of 20 mA/cm², signifying outstanding stability in the long-term HER/OER process. All of the results indicate that the ZNCP NWAs/NF structure could be a highly promising candidate catalyst for overall water splitting in an alkaline environment.

To create fully solar-powered uninterrupted overall water-splitting systems, a self-driven overall water-splitting system was built by integrating a PSSC, Ni-Zn batteries and an overall water-splitting device, with the overall water-splitting device powered by a PSSC during the day and by fully solar-charged Ni-Zn batteries at night. Figures 5a and 5b demonstrate voltage-time curves of the two-electrode overall water-splitting device and two series-connected Ni-Zn batteries over 24 h, respectively. The left inset of Figure 5a shows that the PSSC is connected in series with two series-connected Ni-Zn batteries and an overall water-splitting device during the day (0-12 h), and the corresponding digital image is presented in Figure S16. The PSSC can provide a stable bias of 1.97 V on the two-electrode overall water-splitting device for 12 h, indicating the successful operation of overall water splitting. Simultaneously, the PSSC can also charge two series-connected Ni-Zn batteries, which are fully charged after 12 h (the red line of Figure 5b). At night, the overall water-splitting device is powered by the as-obtained fully solar-charged series-connected Ni-Zn batteries (the right inset of Figure 5a), and the corresponding digital image is shown in Figure S17. The overall water-splitting device, driven by two series-connected Ni-Zn batteries, has a stable working voltage of 1.93 V over 12 h. Moreover, the two ZCNP NWAs/NF electrodes show the

formation of a substantial number of bubbles, indicating that the solar-charged, series-connected Ni-Zn batteries can successfully drive the overall water-splitting device all night. Furthermore, the corresponding discharging curve (dark cyan) is presented in Figure 5b, which maintains the discharge plateau, thus demonstrating that our rechargeable Ni-Zn batteries can store enough solar energy. The generated O₂ and H₂ during the self-powered water-splitting process water splitting in 24 h were further collected and measured by gas chromatography. The typical curve, shown in Figure S18, clearly shows that the ratio of O₂ to H₂ is very close to the theoretical value of 1:2 for overall water splitting. These results confirm the successful fabrication of a fully solar-powered uninterrupted overall water-splitting system, which can be widely used in the field of clean and renewable energy.

3. Conclusion

In summary, we have successfully assembled an integrated overall water-splitting system consisting of solar cells, Ni-Zn batteries and ZNCP electrocatalysts to achieve 24-hour overall water splitting. In particular, the silicon-based solar cells enable the charging of the Ni-Zn batteries for energy storage and provide a steady voltage for electrocatalysis during the day. More importantly, the ultrahigh-capacity Ni-Zn batteries provide a steady output voltage of 1.75 V for overall water electrocatalysis splitting at night, depending on the degree of self-driven energy conversion. Therefore, we believe that using such uninterrupted solar-to-hydrogen conversion and storage systems could provide important opportunities for the development and application of renewable energy, which will accelerate the sustainable development of green energy management.

4. Experimental section

Preparation of ZNCO@Ni(OH)₂ NWAs/NF: ZNCO nanowire arrays grown on an NF were prepared by a hydrothermal method and subsequent annealing. First, a piece of NF (2 cm* 4 cm) was pretreated with 3 M hydrochloric acid solution for 15 min to remove nickel oxide from the surface and washed with acetone and deionized water several times. Then, 3 mmol of Co(NO₃)₂·6H₂O, 1.5 mmol of Ni(NO₃)₂·6H₂O, 1.5 mmol of Zn(NO₃)₂·6H₂O, 6 mmol of CO(NH₂)₂, and 2 mmol of NH₄F were dissolved in 40 mL of deionized water. After stirring for 30 min, the NF was placed in the mixed solution and transferred to a 50 mL Teflon-lined stainless steel autoclave at a temperature of 130 °C. The reaction was maintained for 5 h. After cooling to room temperature, the resulting NF was rinsed with deionized water and dried at 60 °C in air for 12 h. Next, the obtained sample was annealed into ZNCO NWAs/NF in an air atmosphere at 350 °C for 4 h. Subsequently, 76 mmol NiSO₄, 14.8 mmol K₂S₂O₈ and 10 mL of aqueous ammonia (28%) were dissolved in 200 mL of deionized water under vigorous stirring. The ZNCO NWAs/NF was suspended in the stirred mixed solution for 30 min. Finally, the ZNCO@Ni(OH)₂ NWAs/NF was obtained after washing with deionized water and dried at 60 °C overnight.

Preparation of ZNCP NWAs/NF: The ZNCO NWAs/NF was prepared by the above-described method. For phosphidation, 1.0 g NaH₂PO₂ and a piece of ZNCO NWAs/NF were placed at the centre and on the downstream side of the furnace, respectively. The furnace was heated to 350 °C at a heating rate of 5 °C/min and held at that temperature for 2 h.

Assembling the aqueous Ni-Zn batteries: For battery assembly, the ZNCO@Ni(OH)₂ NWAs/NF and Zn plates served as the cathode and anode of the Ni-Zn batteries, respectively. An aqueous ZnO-saturated 3 M KOH solution was used as the electrolyte.

Supporting Information ((delete if not applicable))

Supporting Information is available from the Wiley Online Library or from the author.

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References

- [1] F. Wang, O. Borodin, T. Gao, X. Fan, W. Sun, F. Han, A. Faraone, J.A. Dura, K. Xu, C. Wang, *Nat. Mater.* **2018**, 17, 543.
- [2] D. Kundu, B.D. Adams, V. Duffort, S.H. Vajargah, Nazar, L.F. Nazar, *Nat. Energy* **2016**, 1, 16119.

- [3] H. Pan, Y. Shao, P. Yan, Y. Cheng, K.S. Han, Z. Nie, C. Wang, J. Yang, X. Li, P. Bhattacharya, K.T. Mueller, *Nat. Energy* **2016**, 1, 16039.
- [4] W. Chen, G. Li, A. Pei, Y. Li, L. Liao, H. Wang, J. Wan, Z. Liang, G. Chen, H. Zhang, J. Wang, Y. Cui, *Nat. Energy* **2018**, 3, 428.
- [5] R. Cariou, J. Benick, F. Feldmann, O. Höhn, H. Hauser, P. Beutel, N. Razek, M. Wimplinger, B. Bläsi, D. Lackner, M. Hermle, *Nat. Energy* **2018**, 3, 326 .
- [6] H. Jinno, K. Fukuda, X. Xu, S. Park, Y. Suzuki, M. Koizumi, T. Yokota, I. Osaka, K. Takimiya, T. Someya, *Nat. Energy* **2017**, 2, 780.
- [7] J. Lin, M. Lai, L. Dou, C.S. Kley, H. Chen, F. Peng, J. Sun, D. Lu, S.A. Hawks, C. Xie, F. Cui, *Nat. Mater.* **2018**, 17, 261.
- [8] N. Zhang, F. Cheng, J. Liu, L. Wang, X. Long, X. Liu, F. Li, J. Chen, *Nat. Commun* **2017**, 8, 405 .
- [9] A.M. Zamarayeva, A.E. Ostfeld, M. Wang, J.K. Duey, I. Deckman, B.P. Lechêne, G. Davies, D.A. Steingart, A.C. Arias, *Sci. Adv.* **2017**, 3, e1602051.
- [10] F. Wan, L. Zhang, X. Dai, X. Wang, Z. Niu, J. Chen, *Nat. Commun* **2018**, 9.
- [11] J. Chen, Y. Huang, N. Zhang, H. Zou, R. Liu, C. Tao, X. Fan, Z.L. Wang, *Nat. Energy* **2016**, 1, 16138 .
- [12] P. He, G. Zhang, X. Liao, M. Yan, X. Xu, Q. An, J. Liu, L. Mai, *Adv. Energy Mater.* **2018**, 8, 1702463.
- [13] P. Hu, T. Zhu, X. Wang, X. Wei, M. Yan, J. Li, W. Luo, W. Yang, W. Zhang, L. Zhou, Zhou, Z., Zhou, *Nano Lett.* **2018**, 18, 1758-1763 .

- [14] H. Li, C. Han, Y. Huang, Y. Huang, M. Zhu, Z. Pei, Q. Xue, Z. Wang, Z. Liu, Z. Tang, Y. Wang, *Energy Environ. Sci.* **2018**, 11, 941-951.
- [15] Z. Ren, J. Yu, Y. Li, C. Zhi, *Adv. Energy Mater.* **2018**, 8, 1702467.
- [16] Z. Wen, M.H. Yeh, H. Guo, J. Wang, Y. Zi, W. Xu, J. Deng, L. Zhu, X. Wang, C. Hu, L. Zhu, *Sci. Adv.* **2016**, 2, e1600097.
- [17] Y. Zeng, X. Zhang, Y. Meng, M. Yu, J. Yi, Y. Wu, X. Lu, Y. Tong, *Adv. Mater.* **2017**, 29, 1700274.
- [18] B.Q. Li, S.Y. Zhang, B. Wang, Z.J. Xia, C. Tang, Q. Zhang, *Energy Environ. Sci.* **2018**.
- [19] X. Ren, H. Fan, C. Wang, J. Ma, H. Li, M. Zhang, S. Lei, W. Wang, *Nano Energy* **2018**, 50, 562-570 .
- [20] Y. Qiu, W. Liu, W. Chen, G. Zhou, P.C. Hsu, R. Zhang, Z. Liang, S. Fan, Y. Zhang, Y. Cui, *Sci. Adv.* **2016**, 2, e1501764 .
- [21] J. Qi, W. Zhang, R. Cao, *Adv. Energy Mater.* **2018**, 8, 1701620.
- [22] Y. Gu, S. Chen, J. Ren, Y.A. Jia, C. Chen, S. Komarneni, D. Yang, X. Yao, *ACS Nano* **2018**, 12, 245-253.
- [23] X. Jia, Y. Zhao, G. Chen, L. Shang, R. Shi, X. Kang, G.I. Waterhouse, L.Z. Wu, C.H. Tung, T. Zhang, *Adv. Energy Mater.* **2016**, 6, 1502585.
- [24] J. Zheng, X. Chen, X. Zhong, S. Li, T. Liu, G. Zhuang, X. Li, S. Deng, D. Mei, J.G. Wang, *Adv. Funct. Mater.* **2017**, 27, 1704169.
- [25] Y. Xin, X. Kan, L.Y. Gan, Z. Zhang, *ACS Nano* **2017**, 11, 10303-10312.

- [26] G. Anandhababu, Y. Huang, D.D. Babu, M. Wu, Y. Wang, *Adv. Funct. Mater.* **2018**, 28, 1706120.
- [27] Y. Shabangoli, M.S. Rahmanifar, M.F. El-Kady, A. Noori, M.F. Mousavi, R.B. Kaner, *Energy Storage Mater.* **2018**, 11, 282-293.
- [28] P. Liu, D. Gao, W. Xiao, L. Ma, K. Sun, P. Xi, D. Xue, J. Wang, *Adv. Funct. Mater.* **2018**, 28, 1706928.
- [29] H. Li, Q. Li, P. Wen, T.B. Williams, S. Adhikari, C. Dun, C. Lu, D. Itanze, L. Jiang, D.L. Carroll, G.L. Donati, *Adv. Mater.* **2018**, 30, 1705796.
- [30] J. Yin, Y. Li, F. Lv, M. Lu, K. Sun, W. Wang, L. Wang, F. Cheng, Y. Li, P. Xi, S. Guo, *Adv. Mater.* **2017**, 29, 1704681.
- [31] J. Yang, X. Wang, B. Li, L. Ma, L. Shi, Y. Xiong, H. Xu, *Adv. Funct. Mater.* **2017**, 27, 1606497.
- [32] J. Liu, C. Guan, C. Zhou, Z. Fan, Q. Ke, G. Zhang, C. Liu, J. Wang, *Adv. Mater.* **2016**, 28, 8732-8739.
- [33] Y. Zeng, Y. Meng, Z. Lai, X. Zhang, M. Yu, P. Fang, M. Wu, Y. Tong, X. Lu, *Adv. Mater.* **2017**, 29, 1702698.
- [34] C. Xu, J. Liao, C. Yang, R. Wang, D. Wu, P. Zou, Z. Lin, B. Li, F. Kang, C.P. Wong, *Nano Energy* **2016**, 30, 900-908.
- [35] Y. Huang, W.S. Ip, Y.Y. Lau, J. Sun, J. Zeng, N.S.S. Yeung, W.S. Ng, H. Li, Z. Pei, Q. Xue, Y. Wang, *ACS Nano* **2017**, 11, 8953-8961.

- [36] M. Gong, Y. Li, H. Zhang, B. Zhang, W. Zhou, J. Feng, H. Wang, Y. Liang, Z. Fan, J. Liu, H. Dai, *Energy Environ. Sci.* **2014**, 7, 2025-2032.
- [37] Zhang, W. Xu, J. Sun, Z. Pan, J. Zhao, X. Wang, J. Zhang, P. Man, J. Guo, Z. Zhou, B. He, *Nano Lett.* **2017**, 17, 7552-7560.
- [38] Y. Zeng, Z. Lin, Z. Wang, M. Wu, Y. Tong, X. Lu, *Adv. Mater.* **2018**, 30, 1707290.
- [39] C. Guan, W. Zhao, Y. Hu, Q. Ke, X. Li, H. Zhang, J. Wang, *Adv. Energy Mater.* **2016**, 6, 1601034.
- [40] X. Wu, Z. Lu, W. Zhu, Q. Yang, G. Zhang, J. Liu, X. Sun, *Nano Energy* **2014**, 10, 229-234.
- [41] W. Liu, K. Du, L. Liu, J. Zhang, Z. Zhu, Y. Shao, M. Li, *Nano Energy* **2017**, 38, 576-584.
- [42] L. Yu, H. Zhou, J. Sun, F. Qin, D. Luo, L. Xie, F. Yu, J. Bao, Y. Li, Y. Yu, S. Chen, *Nano Energy* **2017**, 41, 327-336.
- [43] Y. Zhang, Q. Shao, S. Long, X. Huang, *Nano Energy* **2018**, 45, 448-455.

Figure 2 Characterization and electrochemical performance of the Ni-Zn battery. (a) SEM image of ZNCO@Ni(OH)₂ nanowire arrays. (b) SEM image of single ZNCO@Ni(OH)₂ nanowire. (c) Discharge curves of ZNCO@Ni(OH)₂ nanowires under different current densities. (d) Schematic of the aqueous Ni-Zn battery. (e) GCD curves of the as-assembled Ni-Zn battery under different current densities. (f) Areal energy and power densities of our Ni-Zn battery.

Figure 3 Solar-charged Ni-Zn battery. (a) Schematic solar-charged Ni-Zn battery. (b) Current-voltage characteristic curve of PSSC under AM 1.5 illumination. (c) Open-circuit voltage and short-circuit current of the PSSC device under AM 1.5 illumination over 12 h. (d) Ni-Zn battery charged under different light intensities for the same duration of illumination. (e) Light-charge and galvanostatic discharge performance of the solar-charged Ni-Zn battery.

Figure 4 Characterization and electrocatalytic performance of the ZNCP NWAs. (a) SEM image of ZNCP NWAs. (b) TEM image of single ZNCP NWAs. (c) EDS mapping images of ZNCP NWAs. (d) Polarization curves of ZNCP/NF for HER and OER in 1 M KOH solution at a scan rate of 5 mV/s. (e) Polarization curves of ZNCP/NF for overall water splitting in 1 M KOH solution at a scan rate of 5 mV/s (inset: Schematic diagram of overall water splitting). (f) Chronopotentiometric curve of ZNCP/NF for overall water splitting with a current density of 20 mA/cm².

Figure 5 Fully solar-powered uninterrupted, overall water-splitting system. (a) Voltage-time curve of self-driven overall water splitting powered by a PSSC (0-12 h) and two series-connected solar-charged Ni-Zn batteries (12-24 h). (b) Charging curve of two series-connected Ni-Zn batteries charged by a PSSC (0-12 h) and the discharging curve of the Ni-Zn batteries during the self-driven overall water-splitting process (12-24 h).