



VOPO₄·2H₂O Nanosheet Cathode for Enhanced Sodium Storage

Xianghua Zhang¹, Dan Yang¹, Weiling Liu², Yuezhan Feng³, Xianhong Rui^{1*} and Yan Yu^{4,5,6*}

¹ School of Materials and Energy, Guangdong University of Technology, Guangzhou, China, ² School of Materials Science and Engineering, Nanyang Technological University, Singapore, Singapore, ³ Key Laboratory of Materials Processing and Mold (Zhengzhou University), Ministry of Education, Zhengzhou University, Zhengzhou, China, ⁴ Hefei National Laboratory for Physical Sciences at the Microscale, Department of Materials Science and Engineering, Key Laboratory of Materials for Energy Conversion, Chinese Academy of Sciences (CAS), University of Science and Technology of China, Hefei, China, ⁵ Dalian National Laboratory for Clean Energy (DNL), Chinese Academy of Sciences, Dalian, China, ⁶ State Key Laboratory of Fire Science, University of Science and Technology of China, Hefei, China

OPEN ACCESS

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*Correspondence:

Xianhong Rui
xhru@gdut.edu.cn
Yan Yu
yanyumse@ustc.edu.cn

Specialty section:

This article was submitted to
Electrochemical Energy Conversion
and Storage,
a section of the journal
Frontiers in Energy Research

Received: 19 June 2020

Accepted: 29 July 2020

Published: 19 August 2020

Citation:

Zhang X, Yang D, Liu W, Feng Y,
Rui X and Yu Y (2020) VOPO₄·2H₂O
Nanosheet Cathode for Enhanced
Sodium Storage.
Front. Energy Res. 8:200.
doi: 10.3389/fenrg.2020.00200

Na-ion batteries (SIBs) are anticipated to capture a broad development space in the field of large-scale energy storage due to the abundant sodium resources. High-performance cathode materials are very critical. VOPO₄·2H₂O with a two-dimensional (2D) layered structure is a very promising candidate for SIBs because of its high working voltage and theoretical specific capacity. Herein, a simple one-step reflux method is designed to fabricate a cathode of VOPO₄·2H₂O nanosheets. It exhibits a high average operating potential of ~3.5 V, remarkable specific capacity (e.g., 135 mAh g⁻¹ at 0.05 C), favorable high current charge-discharge ability (e.g., 58 mAh g⁻¹ even at 20 C) as well as extralong cyclability (e.g., 0.026% capacity fading rate for per cycle at 20 C during 1000 cycles). The kinetic analysis implies that the superior sodium storage performance is mainly benefiting from the advantages of unique nanosheet structure, accelerating the rapid Na-ion diffusion.

Keywords: sodium ion battery, cathode material, VOPO₄·2H₂O, nanosheets, high performance

INTRODUCTION

The dramatic growing of the portable electronic technology has stimulated the fast development of rechargeable batteries owing to high safety, low cost, availability, scalability and environmental benignity (Deng et al., 2020; Tang et al., 2020; Xie et al., 2020). As a pioneer, Li-ion batteries (LIBs) have become a leader in commercialization since their high energy densities and stable cycling performance (Tan et al., 2018; Yang et al., 2019, 2020). However, the issues of limited reserves, uneven distribution and high price of lithium resources perplexed their large-scale energy storage applications in future (Wang et al., 2017; Guo et al., 2020). Among the post LIBs, Na-ion batteries (SIBs) have caused wide increasing concern due to the cheap price, rich reserve and even distribution of sodium resources in the crust of the earth (Chen S. et al., 2017; Yu et al., 2019; Zhao et al., 2019). However, the bulkier radius [1.02 (Na⁺) vs. 0.76 Å (Li⁺)] makes the Na-ion diffusion more sluggish than that of Li-ions, resulting in the larger volume change, the lower special capacity and the poorer cyclical stability, which limit the further development of SIBs in large-scale energy storage system (Wang et al., 2018; Liu et al., 2020). Therefore, designing/exploring novel advanced

electrodes for SIBs to facilitate fast Na-ion transfer is the top priority at present (Li C. et al., 2020; Wang B. et al., 2020).

Recently, two-dimensional (2D) layer electrodes have shown the promising electrochemical property due to their unique 2D ion transport corridor, short ion diffusion distance and adjustable interlayer space, which are beneficial to promote the Na-ion insertion/extraction reactions (Huang et al., 2014; Shi et al., 2019; Verma et al., 2019). Among them, 2D hydrated vanadium oxyphosphate (VOPO₄·2H₂O) has received considerable attention as the promising cathode materials for SIBs because of its high redox reaction potential (~3.5 V), high theoretical specific capacity (166 mAh g⁻¹), and various valences reactions (e.g., V⁵⁺ ~V³⁺) (Chen N. et al., 2017; Wang J. et al., 2020; Xiong et al., 2020). For example, the bulk VOPO₄·2H₂O synthesized by Peng et al. (2017) can release a delightful reversible specific capacity of 151 mAh g⁻¹ at the testing rate of 0.1 C. It however displays inferior rate capability (e.g., ~50 mAh g⁻¹ at a high electrical current density of 20 C) and cycling performance (only 51% capacity retention over 500 cycles at 5 C). Another bulk VOPO₄·2H₂O cathode prepared by Zhu's group, which although delivers an acceptable discharge capacity (~140 mAh g⁻¹ at 0.1 C), it shows a poor high current charge-discharge ability with almost no capacity at 5 C (Zhu et al., 2016). This is mainly because of the large bulk morphology, which prolongs the diffusion distance of sodium ions. Thus, it is highly desirable to build nanostructured VOPO₄·2H₂O to enhance the sodium storage kinetics.

In this work, VOPO₄·2H₂O nanosheets (thickness: 20–40 nm) are developed and utilized as the cathode material to enable fast and reversible sodium ion intercalation/deintercalation, so that it exhibited high reversible sodium storage capacity (135 mAh g⁻¹ at 0.05 C), remarkably improved rate capability (58 mAh g⁻¹ even at 20 C) and extralong cycle stability (e.g., capacity retention of 74% at a high rate of 20 C after the 1000th cycle). In addition, the VOPO₄·2H₂O nanosheets also showed rapid Na-ion diffusivities exceeding 1.7×10^{-13} cm² s⁻¹ due to the convenient Na⁺ transport channel provided by the nanosheets structure. The outstanding SIB performance of the VOPO₄·2H₂O nanosheet cathode makes it to be a very popular candidate with increasingly wide utilization in large-scale energy storage system.

MATERIALS AND METHODS

Synthesis of VOPO₄·2H₂O Nanosheets

All reagents were purchased from Sinopharm Chemical Reagent Co., Ltd. (China) and used directly without any treatment. The VOPO₄·2H₂O nanosheets was synthesized by a feasible reflux method. Specifically, 5.0 g of vanadium pentoxide powders (V₂O₅) and 120 mL of deionized water (DI H₂O) were put into a conical flask and then 30 mL of the concentrated phosphoric acid (85% H₃PO₄) was added. The suspension was then refluxed at the heating temperature of 100°C for 18 h under vigorous stirring. After the reaction completed, it takes a little time to cool to room temperature, and the yellow-greenish sample was finally gathered by centrifugation, washing (water, ethanol and acetone), and vacuum drying (60°C for 5 h). For comparison, the

bulk VOPO₄·2H₂O sample was synthesized by a traditional ball milling approach. 5.0 g of V₂O₅, 120 mL of DI H₂O, and 30 mL of 85% H₃PO₄ were accurately weighed and added to the agate jar in proper order. After that, the milling equipment operated along a single orientation with the optimal rotate speed of 500 rpm min⁻¹ for 18 h, and then it was centrifuged, washed and vacuum dried to yield bulk VOPO₄·2H₂O sample. Here, it is worth mentioning that the as-obtained samples were stored in a glove box filled with argon atmosphere.

Characterization

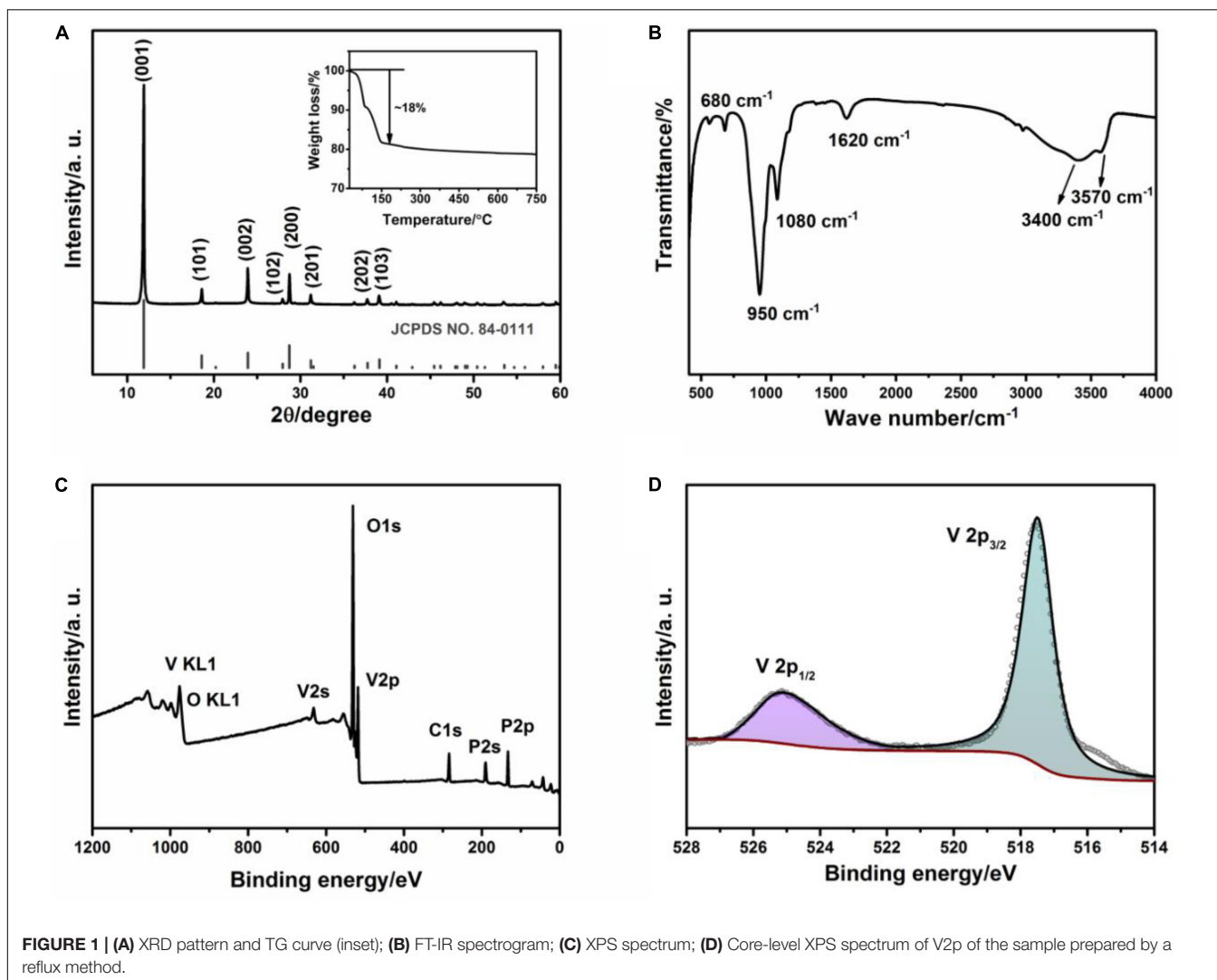
The X-ray diffraction (XRD) patterns were carried out on a Rigaku SmartLab polycrystal X-ray diffraction with Cu K α X-ray source ($\lambda = 1.54056$ Å) scanned in the 2 θ range of 10–60°. The Fourier transform infrared spectroscope (FTIR) was recorded on a UV-3600 Plus spectrometer. The thermal gravimetric analysis (TGA/DSC3+) were tested within the temperature range of 25–750°C in air atmosphere (heating rate: 10°C min⁻¹). The morphology was studied by employing a Hitach SU-8220 field-emission scanning electron microscopy (FESEM) at 10 kV accelerating voltage and a FEI Tecnai G2f20s-twin 200 kV transmission electron microscopy (TEM) instrument.

Electrochemical Measurement

The electrochemical measurements of the as-obtained VOPO₄·2H₂O cathodes were investigated in 2032-type coin cells, which were assembled in an argon-filled glovebox equipment, where both H₂O and O₂ levels were less than 0.1 ppm. For the cathode electrode part, it was prepared by mixing VOPO₄·2H₂O, carbon nanotubes and polyvinylidene fluoride (the mass ratio = 6:3:1) in the N-methyl pyrrolidone solvent, and then the well stirred slurry was coated evenly on an aluminum foil and dried at 60°C in a vacuum oven for 12 h. Na metal was used as the counter electrode. Glass fiber membrane was acted as separator. And a solution of 1 mol L⁻¹ NaClO₄ in propylene carbonate (PC) and ethylene carbonate (EC) (1:1 v/v) with 5% fluoroethylene carbonate (FEC) was selected as electrolyte. The galvanostatic discharge-charge measurements were carried out on NEWARE system within the cutoff voltage window of 2.5–4.3 V versus Na⁺/Na. Electrochemical impedance spectroscopy (EIS) with the testing frequency range of 10⁵ to 10⁻² Hz and cyclic voltammograms (CV) at different scan rates were conducted by the Multi-Autolab M204 electrochemical workstation.

RESULTS AND DISCUSSION

Figure 1A demonstrated the XRD pattern of the as-synthesized sample via applying a reflux method. All the presented diffraction peaks can be well indexed into the tetragonal VOPO₄·2H₂O (JCPDS files no. 84-0111, space group: P4/n) with no detected impurity peak, implying the as-synthesized sample is pure high-crystalline VOPO₄·2H₂O (Zhou et al., 2016). TGA analysis was employed to identify the water content of the as-obtained sample (inset in **Figure 1A**). It is showed a weight loss of ~18% between 25 and 200°C, attributing to the evaporation of the crystal water and the content is determined to be two H₂O molecules per



unit formula of VOPO₄, which is also in good agreement with the data from previous literatures (Zhou et al., 2018; Hyoung et al., 2019). The FTIR spectrum is shown in **Figure 1B**. The vibration peaks in the low wave number region (<800 cm⁻¹) are represented the V–O stretching vibration. And the two intense broad bands at 1080 and 950 cm⁻¹ are ascribed to P–O bond, implying the existence of [PO₄] tetrahedral (Bao et al., 2011). Additionally, the band located at 1620 cm⁻¹ is corresponding to the bending vibration of interlayer water molecules. And two characteristic bands at 3570 and 3400 cm⁻¹ are relative to P–OH stretching vibration and OH stretching vibration of water molecule in VOPO₄·2H₂O, respectively (Zhou et al., 2014). Furthermore, the XPS analysis is also employed to confirm the surface compositions and oxidation state of vanadium in the VOPO₄·2H₂O nanosheets. As illustrated in **Figure 1C**, the P, O, and V elements are found in the XPS profile, consistent with the results obtained from the XRD test. It is worth mentioning that the C1s is used as the standard spectrum for calibrating system error, whose core-level XPS spectrum coupled with that of P 2p and O 1s are shown in **Supplementary Figure S1**. According

to **Figure 1D**, the V 2p core-level shows the binding energies corresponding to V 2p_{2/3} peak and V 2p_{1/2} peak are 517.5 and 525.2 eV, respectively, confirming the main state of V⁵⁺ in the synthesized sample (Yang et al., 2018).

The morphology and detailed microstructure of the sample prepared by a reflux method were explored by field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM). As presented in FESEM images in **Figures 2a–c**, the as-prepared sample shows numerous smooth-surfaced homogenous nanosheets with an approximately thickness of 20–40 nm integrated in an interconnected framework, which can stimulate fast Na-ions transportation and electrons diffusion. The TEM images (**Figures 2d,e**) further reveal the ultrathin feature of nanosheets as indicated by the almost transparent character of the nanosheets. The detailed crystalline structure of VOPO₄·2H₂O nanosheets was ulteriorly explored by high-resolution transmission electron microscope (HRTEM). As displayed in **Figure 2f**, the crystalline lattice distance of 0.351 and 0.319 nm is indexed to the (002) and (102) planes of the tetragonal VOPO₄·2H₂O, respectively.

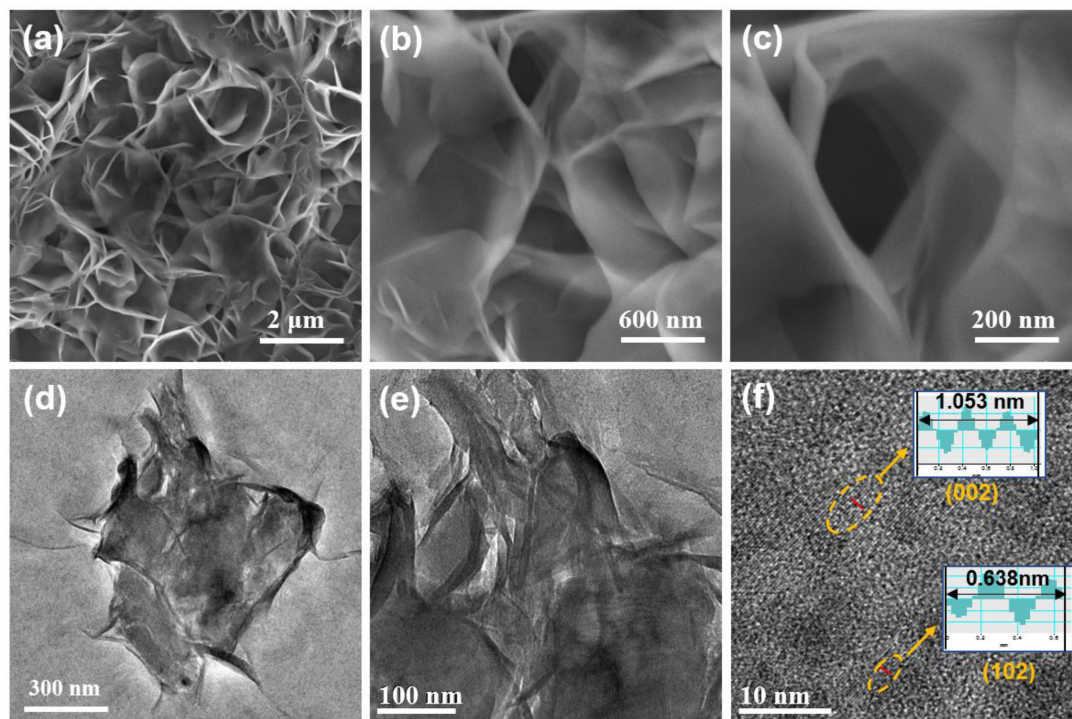


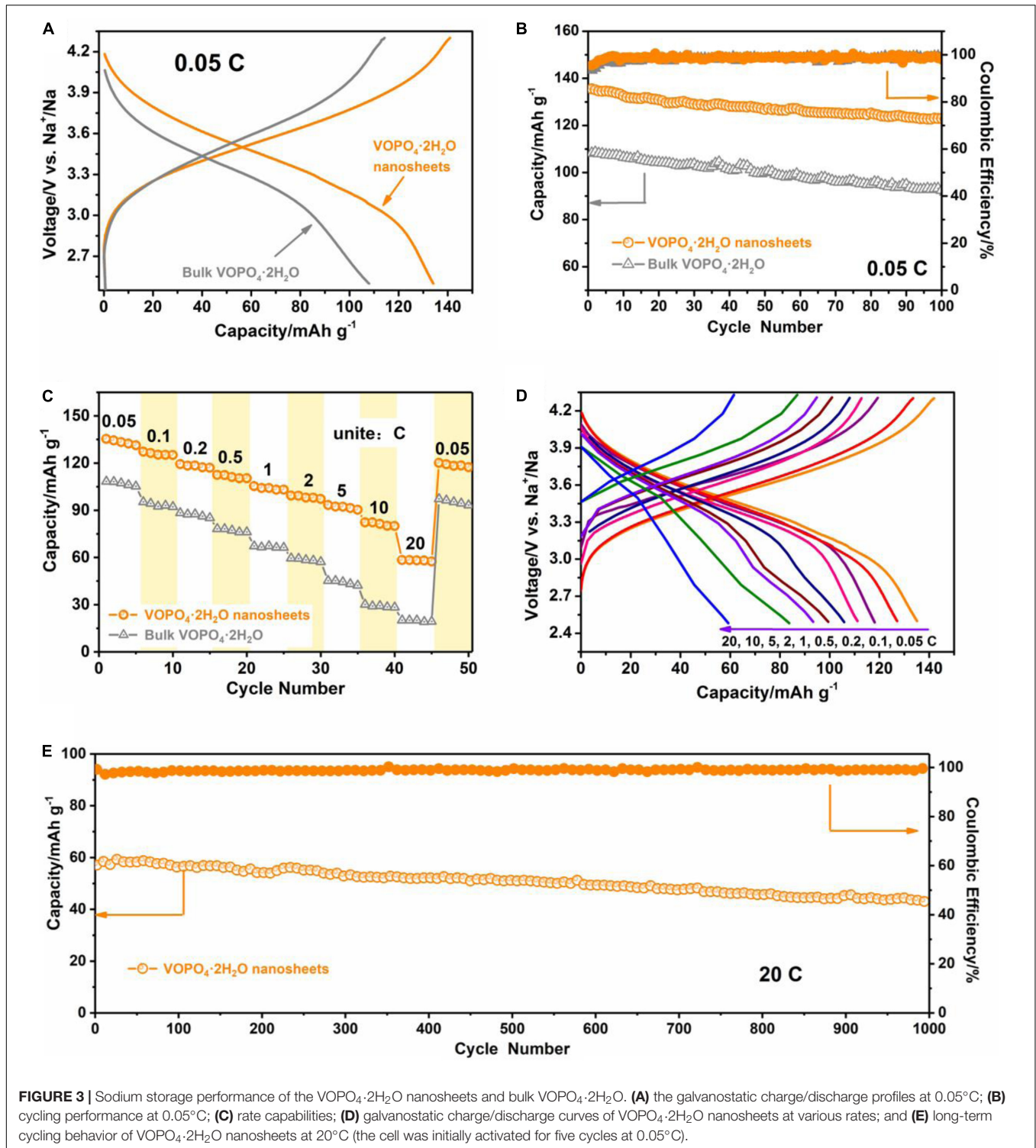
FIGURE 2 | FESEM images of the VOPO₄·2H₂O nanosheets with different magnifications (a–c); TEM images of the VOPO₄·2H₂O nanosheets (d,e); HRTEM image of the VOPO₄·2H₂O nanosheets (f).

For comparison, the bulk VOPO₄·2H₂O sample was prepared by a ball milling method and its intrinsic basic characterizations are investigated and shown in **Supplementary Figures S2–S6**. It is evident that the SEM images of bulk VOPO₄·2H₂O control sample display an irregular large chunk morphology with the size of >2 μm, accompanied by obvious agglomeration (**Supplementary Figure S6**).

The electrochemical behavior of VOPO₄·2H₂O nanosheets and bulk VOPO₄·2H₂O as SIB cathodes were evaluated in a voltage window of 2.5–4.3V (vs. Na⁺/Na) by the galvanostatic charge and discharge test. As shown in **Figure 3A**, both samples exhibit the S-type charge/discharge profiles with an average working potential of ~3.5 V (vs. Na⁺/Na), corresponding to the V⁴⁺/V⁵⁺ redox couple (Peng et al., 2017). The VOPO₄·2H₂O nanosheets display a specific discharge capacity of 135 mAh g⁻¹ at a low current density of 0.05 C, which is remained at 123 mAh g⁻¹ after 100 cycles with a 91% capacity retention (**Figure 3B**). During cycling, the Coulombic efficiency is always kept at ~100%, suggesting a good reversibility. However, the specific discharge capacity of the bulk VOPO₄·2H₂O is only 109 mAh g⁻¹ at 0.05 C, and a relatively low capacity retention ratio of 85% after the 100th cycle is illustrated. The inferior performance of the bulk material is mainly due to its large size, which makes the longer Na-ion diffusion path and some of the inner part of the active materials may not participate in the electrochemical reaction, resulting in the lower reversible specific capacity and quicker capacity decay. More importantly, owing to the unique nanosheet structure, the VOPO₄·2H₂O

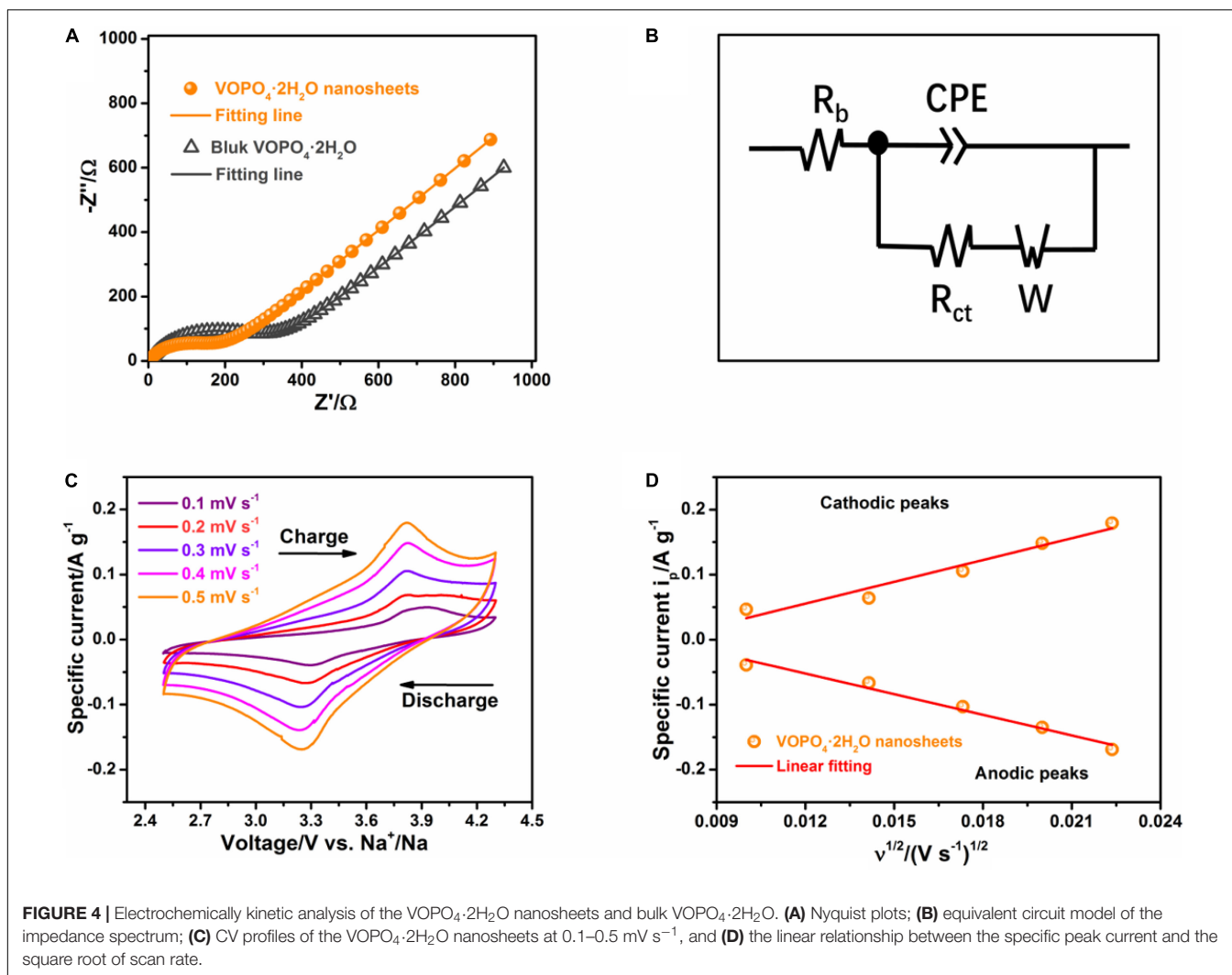
nanosheets exhibit a remarkably high rate capability. As displayed in **Figure 3C**, the specific discharge capacities of 127, 117, 111, 105, 99, and 93 mAh g⁻¹ can be available at rates of 0.1, 0.2, 0.5, 1, 2, and 5 C, respectively. And even at high rates of 10 and 20 C, the reversible capacities actually reach 82 and 58 mAh g⁻¹, respectively. And the discharge capacity can still be back to 119 mAh g⁻¹ when the rate is returned to 0.05 C. In contrast, the rate capability of the bulk VOPO₄·2H₂O is much poor, which barely delivers 45 and 29 mAh g⁻¹ at 5 and 10 C, respectively, and even almost no capacity at a high rate of 20 C. Meanwhile, **Figure 3D** shows the charge-discharge curves of VOPO₄·2H₂O nanosheets cathode at various current rates. It is observed that there is more and more obvious polarization phenomenon with increasing current rate, but the general S-type shape of the curves are still maintained, implying a favorable electrochemical stability of the VOPO₄·2H₂O nanosheets as cathode material for SIBs. Moreover, the long-term cyclability of VOPO₄·2H₂O nanosheets was also evaluated at 20 C (**Figure 3E**). Impressively, a reversible discharge specific capacity of 43 mAh g⁻¹ can be maintained after 1000 cycles with a capacity retention of 74%. As examined by the *ex situ* XRD (**Supplementary Figure S7**) and SEM (**Supplementary Figure S8**), the slightly capacity decay is mainly because of the crystallinity deterioration and nanosheet morphology pulverization. Nevertheless, it is still much better than that of the bulk VOPO₄·2H₂O (i.e., 57% capacity retention over only 300 cycles at 20 C, **Supplementary Figure S9**).

To further highlight the advantages of VOPO₄·2H₂O nanosheets, the electrochemical impedance spectrum



measurement (EIS) and cyclic voltammetry (CV) are conducted to explore the charge transfer kinetics. The impedance spectra of the VOPO₄·2H₂O nanosheets together with the bulk VOPO₄·2H₂O sample were evaluated at the 5th fully discharged state. As displayed in **Figure 4A**, the Nyquist plots are comprised of one intercept-value at high frequency, one semicircle at

intermediate frequency and one inclined line in low frequency area, which are consistent with the external circuit resistance (R_b), the charge transfer resistance (R_{ct}), and the Warburg impedance (W), respectively (Guo et al., 2019). The Nyquist curves are fitted by the equivalent circuit as illustrated in **Figure 4B**, and the fitted impedance parameters indicated



that the R_{ct} -value of the VOPO₄·2H₂O nanosheets (211 Ω) is much smaller than that of bulk VOPO₄·2H₂O sample (332 Ω), implying the better electronic conductivity and faster charge transfer for the VOPO₄·2H₂O nanosheets. **Figure 4C** presented the CV curves of the VOPO₄·2H₂O nanosheets at diverse scan rate from 0.1 to 0.5 mV s⁻¹. Obviously, the CV curves exhibited comparable shapes and gradually increased peak intensity along with the increase of scanning rates. And a pair of redox peaks is attributed to the V⁴⁺/V⁵⁺ redox couple reaction, being consistent with the previous literature (Zhu et al., 2016). In addition, the appearance diffusion coefficients of Na⁺ (D_{Na^+}) in VOPO₄·2H₂O cathodes are also investigated on the basis of the CV technique and the Randles-Sevchik Equation (Li Q. et al., 2020):

$$i_p = (2.65 \times 10^5) n^{3/2} S D_{Na^+}^{1/2} C_{Na^+} \nu^{1/2}$$

where i_p is the specific peak current, n is the number of electron transferred, S is the active surface area of the cathode, the concentration of Na-ions in the VOPO₄·2H₂O is represented by C_{Na^+} , and ν is scan rate. D_{Na^+} is determined by the

slope of fitting linear of $i_p - \nu^{1/2}$. As displayed in **Figure 4D** and **Supplementary Figure S10**, a linear relationship between the i_p and the square root of the scan rate $\nu^{1/2}$ is found for both VOPO₄·2H₂O electrodes. Based on the slope value, the D_{Na^+} of VOPO₄·2H₂O nanosheets is determined to be $\sim 1.7 \times 10^{-13}$ cm² s⁻¹, which is one magnitude larger than that of the bulk VOPO₄·2H₂O sample ($\sim 1.9 \times 10^{-14}$ cm² s⁻¹), indicating the rapid Na⁺ extraction/insertion reaction kinetics of the VOPO₄·2H₂O nanosheets.

CONCLUSION

In summary, a simple one-step reflux method was employed to synthesize the novel VOPO₄·2H₂O nanosheets (thickness: 20–40 nm), which can enhance the Na-ion diffusion kinetics. As a result, the VOPO₄·2H₂O nanosheets displayed a high average operating voltage (~ 3.5 V), gratifying reversible capacity (e.g., 135 mAh g⁻¹ at 0.05 C), remarkably improved rate capability (e.g., 58 mAh g⁻¹ even at 20 C) and excellent

cyclic stability (e.g., 74% capacity retention at 20 C over 1000 cycles). The outstanding electrochemical performance of the VOPO₄·2H₂O nanosheets makes it a promising cathode material in rechargeable SIBs.

DATA AVAILABILITY STATEMENT

All datasets generated for this study are included in the article/**Supplementary Material**, further inquiries can be directed to the corresponding author/s.

AUTHOR CONTRIBUTIONS

XR and YY directed the project. XZ, DY, WL, and YF performed the experiment, analyzed the data, and wrote the manuscript. All authors contributed to the article and approved the submitted version.

REFERENCES

- Bao, C., Guo, Y., Song, L., Lu, H., Yuan, B., and Hu, Y. (2011). Facile synthesis of Poly(vinyl alcohol)/ α -titanium phosphate nanocomposite with markedly enhanced properties. *Ind. Eng. Chem. Res.* 50, 11109–11116. doi: 10.1021/ie200700t
- Chen, N., Zhou, J., Kang, Q., Ji, H., Zhu, G., Zhang, Y., et al. (2017). Amorphous Vanadyl Phosphate/graphene composites for high performance supercapacitor electrode. *J. Power Sources* 344, 185–194. doi: 10.1016/j.jpowsour.2017.01.119
- Chen, S., Wu, C., Shen, L., Zhu, C., Huang, Y., Xi, K., et al. (2017). Challenges and perspectives for NASICON-Type electrode materials for advanced sodium-ion batteries. *Adv. Mater.* 29:1700431. doi: 10.1002/adma.201700431
- Deng, C., Xie, X., Han, J., Tang, Y., Gao, J., Liu, C., et al. (2020). A sieve-functional and uniform-porous kaolin layer toward stable zinc metal anode. *Adv. Funct. Mater.* 30:2000599. doi: 10.1002/adfm.202000599
- Guo, C., Zhang, W., Liu, Y., He, J., Yang, S., Liu, M., et al. (2019). Constructing CoO/Co₃S₄ heterostructures embedded in n-doped carbon frameworks for high-performance sodium-ion batteries. *Adv. Funct. Mater.* 29:1901925. doi: 10.1002/adfm.201901925
- Guo, X., Zhou, J., Bai, C., Li, X., Fang, G., and Liang, S. (2020). Zn/MnO₂ battery chemistry with dissolution-deposition mechanism. *Mater. Today Energy* 16:100396. doi: 10.1016/j.mtener.2020.100396
- Huang, H. L., Lii, K.-H., and Wang, S. L. (2014). Really understanding layered Vanadyl phosphate hydrates. *J. Chin. Chem. Soc.* 61, 199–206. doi: 10.1002/jccs.201300520
- Hyung, J., Heo, J. W., Chae, M. S., and Hong, S. (2019). Electrochemical exchange reaction mechanism and the role of additive water to stabilize the structure of VOPO₄·2H₂O as a Cathode material for potassium-ion batteries. *ChemSuschem* 12, 1069–1075. doi: 10.1002/cssc.201802527
- Li, C., Wang, B., Chen, D., Gan, L., Feng, Y., Zhang, Y., et al. (2020). Topotactic transformation synthesis of 2D ultrathin GeS₂ nanosheets toward high-rate and high-energy-density sodium-ion half/full batteries. *ACS Nano* 14, 531–540. doi: 10.1021/acsnano.9b06855
- Li, Q., Chen, D., Tan, H., Zhang, X., Rui, X., and Yu, Y. (2020). 3D porous V₂O₅ architectures for high-rate lithium storage. *J. Energy Chem.* 40, 15–21. doi: 10.1016/j.jechem.2019.02.010
- Liu, S., Zhu, H., Zhang, B., Li, G., Zhu, H., Ren, Y., et al. (2020). Tuning the kinetics of zinc-ion insertion/extraction in V₂O₅ by In situ polyaniline intercalation enables improved aqueous zinc-ion storage performance. *Adv. Mater.* 32:202001113. doi: 10.1002/adma.202001113
- Peng, L., Zhu, Y., Peng, X., Fang, Z., Chu, W., Wang, Y., et al. (2017). Effective interlayer engineering of two-dimensional VOPO₄ nanosheets via controlled

FUNDING

The authors gratefully acknowledge the National Key R&D Research Program of China (Grant No. 2018YFB0905400), National Natural Science Foundation of China (Grant Nos. 51872277, 21606003, 51972067, 51802044, 51925207, and U1910210), the Fundamental Research Funds for the Central Universities (Grant No. WK2060140026), the DNL cooperation Fund, CAS (Grant No. DNL180310), and Guangdong Natural Science Funds for Distinguished Young Scholar (Grant No. 2019B151502039).

SUPPLEMENTARY MATERIAL

The Supplementary Material for this article can be found online at: <https://www.frontiersin.org/articles/10.3389/fenrg.2020.00200/full#supplementary-material>

- organic intercalation for improving alkali ion storage. *Nano Lett.* 17, 6273–6279. doi: 10.1021/acs.nanolett.7b02958
- Shi, H., Song, Y., Qin, Z., Li, C., and Sun, X. (2019). Inhibiting VOPO₄·2H₂O decomposition and dissolution in rechargeable aqueous zinc batteries to promote voltage and capacity stabilities. *Angew. Chem.* 58, 16057–16061. doi: 10.1002/anie.201908853
- Tan, H., Xu, L., Geng, H., Rui, X., Li, C., and Huang, S. (2018). Nanostructured Li₃V₂(PO₄)₃ cathodes. *Small* 14:1800567. doi: 10.1002/sml.201800567
- Tang, Y., Liu, C., Zhu, H., Xie, X., Gao, J., Deng, C., et al. (2020). Ion-confinement effect enabled by gel electrolyte for highly reversible dendrite-free zinc metal anode. *Energy Storage Mater.* 27, 109–116. doi: 10.1016/j.ensm.2020.01.023
- Verma, V., Kumar, S., Manalastas, W. Jr., Zhao, J., and Chila, R. (2019). Layered VOPO₄ as a cathode material for rechargeable zinc-ion battery: effect of polypyrrole intercalation in the host and water concentration in the electrolyte. *ACS Appl. Energy Mater.* 2, 8667–8674. doi: 10.1021/acsaem.9b01632
- Wang, B., Ang, E. H., Yang, Y., Zhang, Y., Geng, H., Ye, M., et al. (2020). Interlayer engineering of molybdenum trioxide toward high-capacity and stable sodium ion half/full batteries. *Adv. Funct. Mater.* 30:2001708. doi: 10.1002/adfm.202001708
- Wang, J., Tan, S., Xiong, F., Yu, R., Wu, P., Cui, L., et al. (2020). VOPO₄·2H₂O as a new cathode material for rechargeable ca-ion batteries. *Chem. Commun.* 56, 3805–3808. doi: 10.1039/d0cc00772b
- Wang, Q., Xu, J., Zhang, W., Mao, M., Wei, Z., Wang, L., et al. (2018). Research progress on vanadium-based cathode materials for sodium ion batteries. *J. Mater. Chem. A* 6, 8815–8838. doi: 10.1039/C8TA01627E
- Wang, Q., Zhang, W., Guo, C., Liu, Y., Wang, C., and Guo, Z. (2017). In situ construction of 3D interconnected FeS@Fe₃C@graphitic carbon networks for high-performance sodium-ion batteries. *Adv. Funct. Mater.* 27:17003390. doi: 10.1002/adfm.201703390
- Xie, X., Liang, S., Gao, J., Guo, S., Guo, J., Wang, C., et al. (2020). Manipulating the Ion-transfer kinetics and interface stability for high-performance zinc metal anodes. *Energy. Environ. Sci.* 13, 503–510. doi: 10.1039/c9ee03545a
- Xiong, P., Zhang, F., Zhang, X., Wang, S., Liu, H., Sun, B., et al. (2020). Strain engineering of two-dimensional multilayered heterostructures for beyond-lithium-based rechargeable batteries. *Nat. Commun.* 11, 3297–3297. doi: 10.1038/s41467-020-17014-w
- Yang, D., Liu, C., Rui, X., and Yan, Q. (2019). Embracing high performance potassium-ion batteries with phosphorus-based electrodes: a review. *Nanoscale* 11, 15402–15417. doi: 10.1039/C9NR05588F
- Yang, H., Xu, G., Wei, X., Cao, J., Yang, L., and Chu, P. K. (2018). Ultrafast hetero-assembly of monolithic interwoven V₂O₅ nanobelts/carbon nanotubes

- architectures for high-energy alkali-ion batteries. *J. Power Sources* 395, 295–304. doi: 10.1016/j.jpowsour.2018.05.081
- Yang, Y., Zhu, H., Xiao, J., Geng, H., Zhang, Y., Zhao, J., et al. (2020). Achieving ultrahigh-rate and high-safety Li⁺ storage based on interconnected tunnel structure in micro-size niobium tungsten oxides. *Adv. Mater.* 32:1905295. doi: 10.1002/adma.201905295
- Yu, Y., Zhang, X., Rui, X., Chen, D., Tan, H. T., Yang, D., et al. (2019). Na₃V₂(PO₄)₃: an advanced cathode for sodium-ion batteries. *Nanoscale* 11, 2556–2576. doi: 10.1039/C8NR09391A
- Zhu, Y., Peng, L., Chen, D., and Yu, G. (2016). Intercalation pseudocapacitance in ultrathin VOPO₄ nanosheets: toward high-rate alkali-ion-based electrochemical energy storage. *Nano Lett.* 16, 742–747. doi: 10.1021/acs.nanolett.5b04610
- Zhao, L., Zhao, H., Du, Z., Wang, J., Long, X., Li, Z., et al. (2019). Delicate lattice modulation enables superior Na storage performance of Na₃V₂(PO₄)₃ as both an anode and cathode material for sodium-ion batteries: understanding the role of calcium substitution for vanadium. *J. Mater. Chem. A* 7, 9807–9814. doi: 10.1039/C9TA00869A
- Zhou, K., Zhang, Q., Wang, B., Liu, J., Wen, P., Gui, Z., et al. (2014). The integrated utilization of typical clays in removal of organic dyes and polymer nanocomposites. *J. Clean. Prod.* 81, 281–289. doi: 10.1016/j.jclepro.2014.06.038
- Zhou, K., Zhou, G., and Yuan, H. (2016). Ultrathin 2D VOPO₄ nanosheets: a novel reinforcing agent in polymeric composites. *RSC Adv.* 6, 100344–100351. doi: 10.1039/C6RA24111E
- Zhou, L., Liu, Q., Zhang, Z., Zhang, K., and Mai, L. (2018). Interlayer-spacing-regulated VOPO₄ Nanosheets with fast kinetics for high-capacity and durable rechargeable magnesium batteries. *Adv. Mater.* 30:1801984. doi: 10.1002/adma.201801984
- Conflict of Interest:** The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.
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