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ORIGINAL REPORT

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Facile preparation of MoP/TiO₂ composite by electrospinning method for sodium ion battery anode

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ABSTRACT

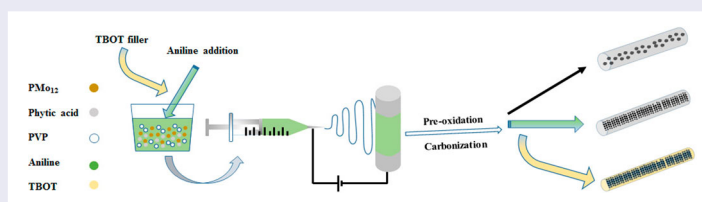
MoP is a promising anode material choice for alkali ion storage ascribed to its superior electrochemical performance. However, severe volume expansion and poor stability limited its output performance. Here, well-dispersed MoP nanoparticles are confined in carbon nanofiber skeleton by facile electrospinning method, further introduction of titania enhances the interfacial reaction and structure stability. As a result, the carbon nanofiber encapsulated MoP/TiO₂ composite exhibited 150 mAh g⁻¹ at 1 A g⁻¹ for 4000 cycles, without obvious capacity decay. The homogenous dispersion and heterostructure construction contribute to its superior performance. This design provides a simple way for the phosphide preparation.

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KEYWORDS

Sodium ion battery; phosphide; electrospinning; heterostructure



Introduction

Featuring earth-abundant and low-cost, sodium ion batteries (SIBs) become competitive for complement or even replacement of LIBs. SIBs share similar working mechanism with LIBs, and close electrode redox potential especially in organic solvent like propylene carbonate [1,2] (−2.71 V for Na and −3.04 V for Li vs. standard hydrogen electrode) exhibits its competitiveness. Obstacles for SIBs lie in the larger radius of Na⁺ compared to Li⁺, leading to sluggish sodium ion diffusion, thus making it harder to find the suitable electrode materials. As an attractive candidate, phosphorus-based materials hold the advantage of high theoretical capacity and low sodium-embedding voltage [3,4]. And the intermediate Na_xM/Na_xP phases formation upon electrochemical cycling of metal phosphide can effectively buffer the volume expansion [5]. Among them, molybdenum phosphide (MoP) has drawn

much attention due to its superior electronic conductivity and great electrochemical activity for alkali metal ions storage [6–11]. Similar to other conversion-type materials, MoP is also puzzled by poor cycling stability and inferior diffusion kinetics.

Building conductive carbon matrix and coupling nanocrystals to construct heterostructures are practical and efficient ways to improve electrochemical performance for the material modification [4,12,13]. Advantages of one-dimensional nanomaterials include large active surface areas, high endurance for deformation stress, shortened ion diffusion path [14]. As a straightforward and versatile fabrication method for the synthesis of one-dimensional nanomaterials, electrospinning has been an appealing option. Particles in nanoscale can effectively alleviate the structure stress brought by the volume expansion during electrochemical cycles [15,16].

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Zeng et al. exploited strong chemical bond of Mo–N to reinforce the charge transfer and structural stability of heterostructure [17,18]. The periodic arrangement of metal ions and organic ligands like MOFs (metal–organic frameworks) can be transformed into metal-based carbon hybrids after calcination, achieving the nanocrystallization and preventing agglomeration among nanoparticles [19–21].

In this work, we provide an aniline-assisted MoP preparation through electrospinning with phytic acid as eco-friendly phosphorous source. Picking Keggin type heteropoly phosphomolybdic acid as starting material and polymerization reaction initiator, the *in-situ* formed PMo_{12} –PANI precursor facilitated the dispersion of nanoparticles in the final product without severe aggregation, and the synthetic procedure is schematically illustrated in Figure 1(a). Through addition of tetrabutyl titanate (TBOT), the cycling life and stability were greatly improved. As a result, the carbon nanofiber encapsulated MoP/TiO₂ composite maintained around 150 mAh g^{−1} at 1 A g^{−1} for 4000 cycles, with superior capacity retention ratio of almost 100%. This work provides a convenient way for the phosphide preparation.

Results and discussion

The morphology and microstructure were investigated by SEM and TEM. As shown in Figure 1(b) and Figure S1a–1b, 1D interconnected nanofibers with diameters around 300–500 nm can be observed in SEM images. Ultrasmall nanoparticles of MP (MoP) were spread over the carbon matrix in Figure S1c, after the addition of aniline, the particles sizes were further reduced and uniformly encapsulated in the carbon nanofiber (MPI, Figure S1d), originated from the dispersion effect of PMo_{12} –PANI precursor [22]. The introduction of titania didn't change the morphology for MPIT sample (Figure 1d), and EDX mapping exhibits well-dispersed Mo/P/N/O/C/Ti element, conforming the filler of TBOT (Figure 1e). The constructed heterostructure interface can be vaguely observed from the marginal part of fiber, which can be assigned to the (200) and (101) planes of TiO₂ and MoP respectively [23,24].

The XRD patterns of MP, MPI and MPIT are presented in Figure 2(a), the MoP phase was well crystallized in all the three samples. While for MPIT, the broaden peaks around 25° and 40° illustrated the introduction of titania [25,26]. The MoP content was calculated to be 62.50%, 55.60% and 49.94% for MP, MPI and MPIT respectively based on thermogravimetric analysis (Figure S2), and the ratio of TiO₂ is about 10.08%. N₂ adsorption and desorption tests (Figure S3) indicated low specific surface area for all three samples

(below 10 m² g^{−1}). Raman peaks (Figure 2b) around 1350 and 1590 cm^{−1} can be assigned to D band (induced by defects or disordered structure) and G band (originating from graphitic sp² carbon) of carbon materials, respectively. After the introduction of aniline, the peak intensity ratio I_D/I_G increased for MPI (0.98) and MPIT (0.99) compared to MP sample (0.86), implying generation of more defects. XPS spectra were collected to study the surface property and element composition. Mo 3d high-resolution spectrum is presented in Figure 2(c), and two peaks around 227.6 and 231 eV verified the existence of MoP. The peak at 228.2 eV/232.7 eV and doublets located at 234.6 eV/235.9 eV are assigned to Mo⁴⁺ and Mo⁶⁺ respectively, illustrating the molybdenum oxides-dominated layers, which is beneficial to the surface faradaic reaction enhancement [8]. Also, the peak with binding energy of 133 eV in P 2p spectrum corresponding to P–O related to surface passivation, while peaks at 129.6 eV/128.8 eV attributed to P 2p_{3/2} and P 2p_{1/2} of MoP (Figure 2d) [9]. In Figure 2(e), intensified Mo–N peaks can be identified after the aniline addition, conforming the transformation of PMo_{12} –PANI precursor. For MPIT sample, Mo–P and Mo–N related peaks diminished in Mo 3d, P 2p and N 1s spectra, implying nearly complete encapsulation of MoP in the carbon nanofiber matrix with the help of TBOT filler. Relatively weak signal of Ti 2p can be detected in Figure 2(f), denoting the introduction of TBOT and thus the titanium dioxide formation. Three peaks at 530.8, 532.4, 532.7 eV indicate the binding energies of O–C=O, O–C, O–P respectively, while the peaks around 284.6, 286.3, 288.8 eV are related to O–C=O, C–O, C–C (Figure S4).

Electrochemical tests for MP, MPI, MPIT were conducted in half-cell in the voltage range of 0.005–3.0 V (vs. Na/Na⁺). When tested at 0.1 mV s^{−1} for three cycles, a distinct reduction peak can be spotted around 0.4 V in the first cathodic scan in Figure 3(a), corresponding to the solid electrolyte interface film forming process. Peaks located at 0.1 V represent the conversion reaction of MoP to Mo and Na₃P [8,11], which is further confirmed by ex-situ XRD tests (Figure S5). In the next two cycles, the curves exhibited well-sustained electrochemical reversibility. The initial charging and discharging curves in Figure 3(b) explained that the irreversible capacity loss mainly comes from the sodiation process, forming solid electrolyte interface layer while consuming large amount of Na⁺, which is consistent with the CV curves. And the capacity mostly contributed from the low voltage conversion reaction. The rate capability is presented in Figure 3(c), the discharging capacity of MPIT sample can be up to 300 mAh g^{−1} under 100 mA g^{−1}, and keep above 100 mAh g^{−1} even under

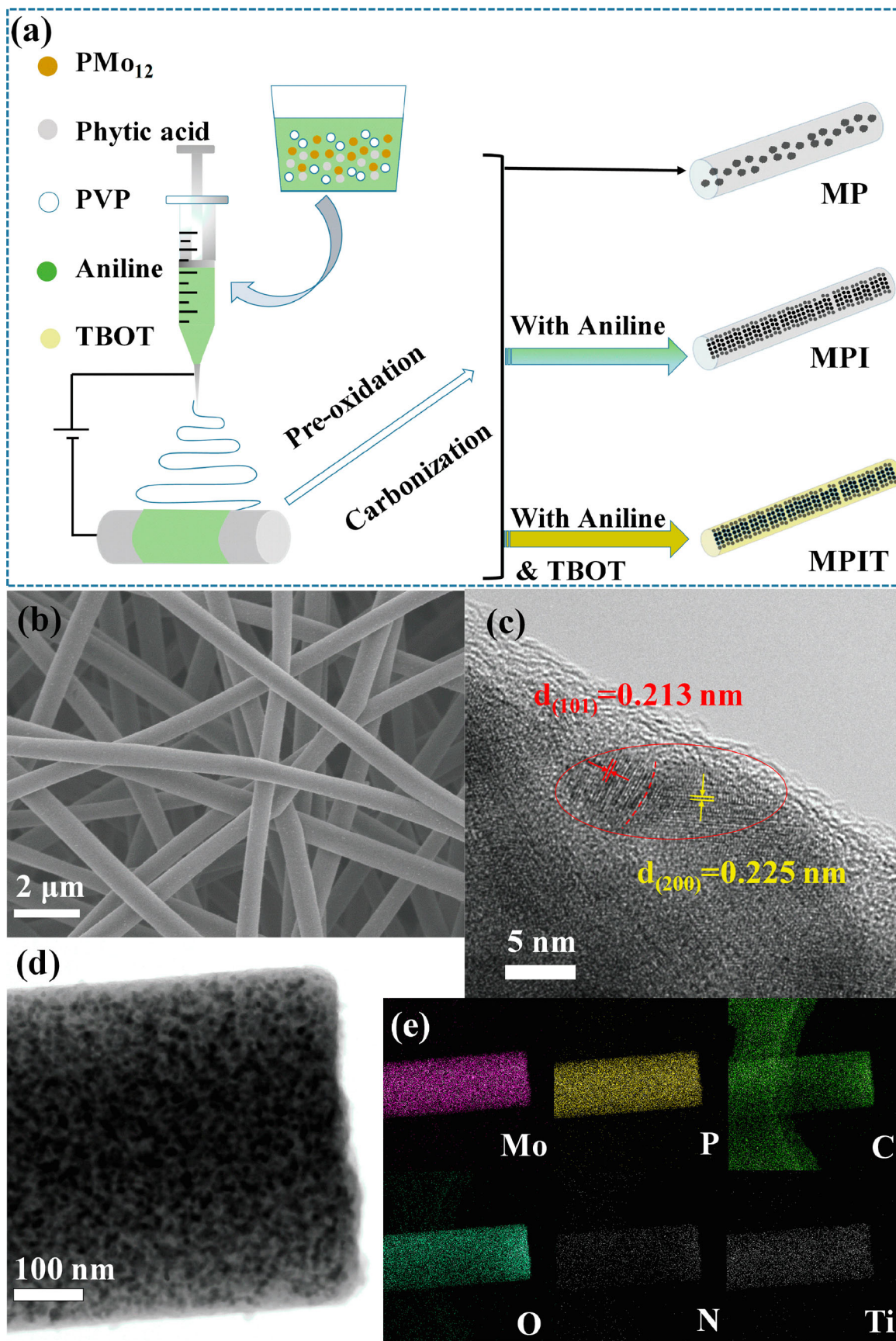


Figure 1. (a) Schematic illustration for the preparation of MP, MPI and MPIT, (b) SEM, (c) HRTEM, (d) TEM photo of MPIT, (e) EDX element mapping for MPIT.

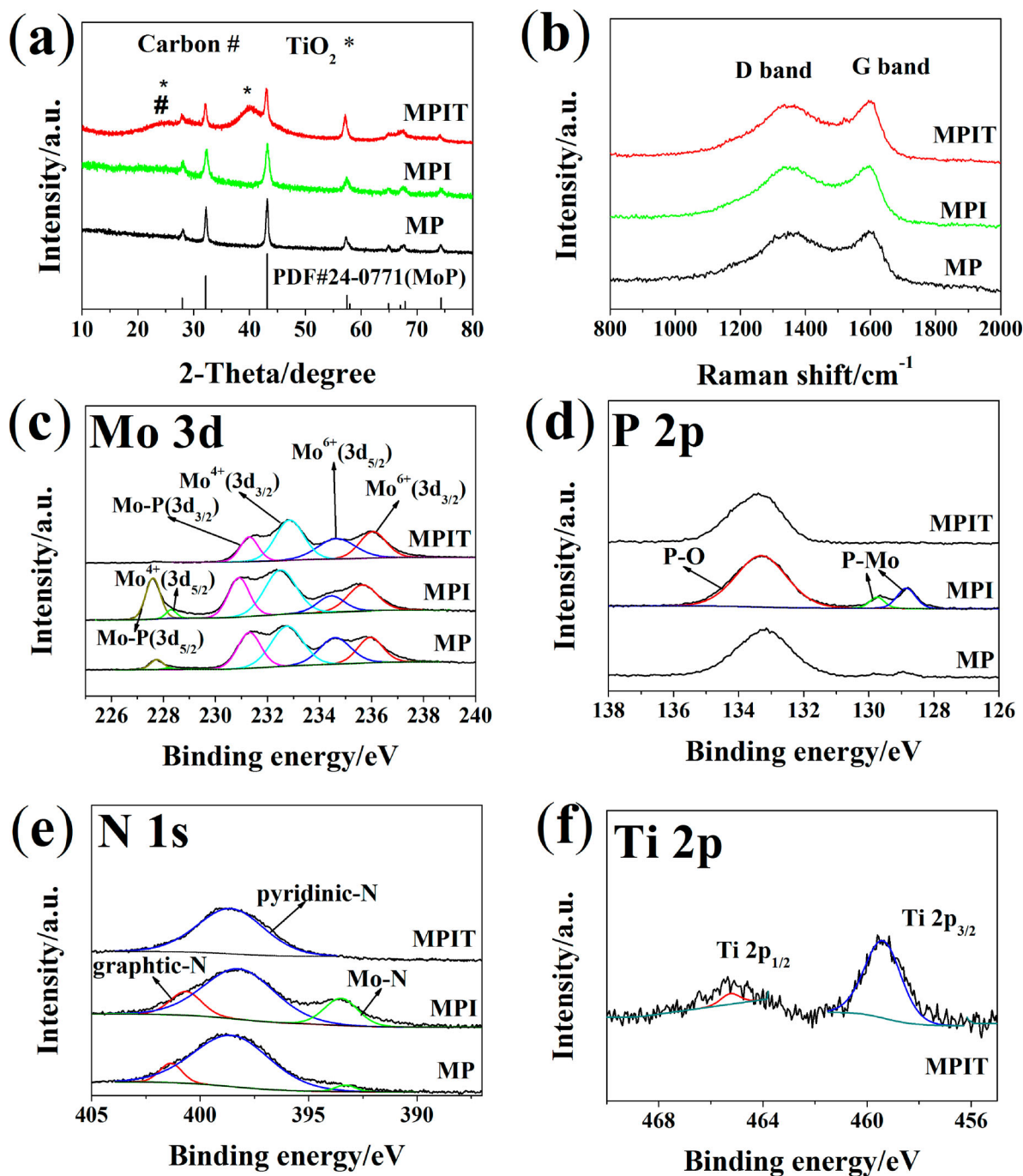


Figure 2. (a) XRD patterns, (b) Raman spectra. High-resolution XPS spectra, (c) Mo 3d, (d) P 2p, (e) N 1s. (f) Ti 2p of MPIT.

current density of 5 A g⁻¹, illustrating the interfacial charge transfer promotion after the heterostructure construction. What's more, the capacity can retain above 220 mAh g⁻¹ when the current density switched back to 200 mA g⁻¹. In comparison, MP and MPI displayed around 200 mAh g⁻¹ at 100 mA g⁻¹ with relatively poor rate capability. Long-term cycling stability was tested at 1 A g⁻¹ and shown in Figure 3(e), the MP sample display capacity of 100 mAh g⁻¹ and decayed rapidly after 1000

cycles, while the MPI manifested better performance ascribed to the positive effect of well-dispersed ultra-small nanoparticle. Surprisingly, the MPIT can retain around 150 mAh g⁻¹ for 4000 cycles with relatively slow fading rate, illustrating the well encapsulation of titania filler, the volume strain got greatly relieved. In Figure 3(f), electrochemical impedance spectroscopy (EIS) collected at open circuit voltage shows that MoP has a small electrochemical resistance, manifesting its

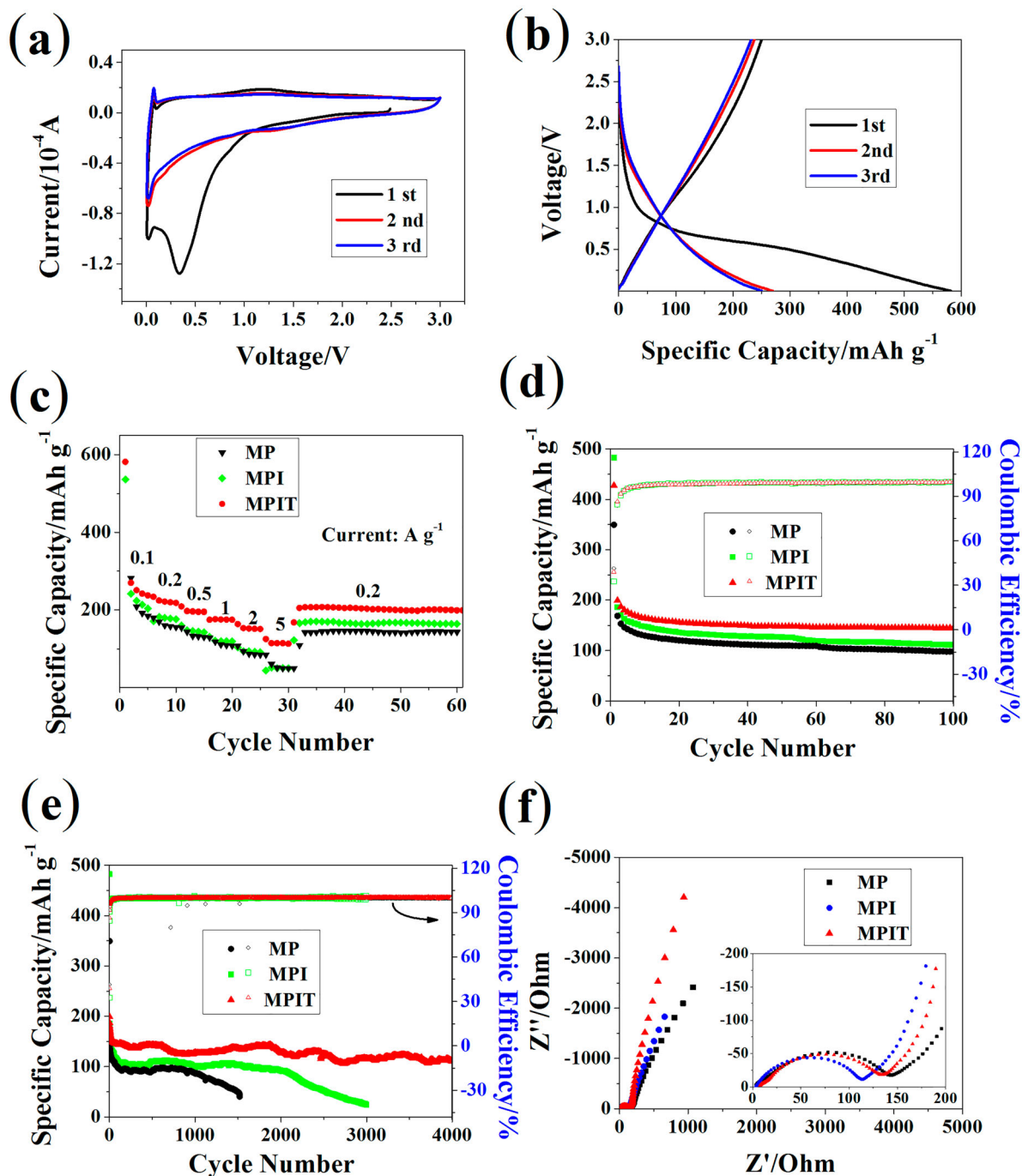


Figure 3. Sodium ion storage properties. (a) CV graphs of MPIT at 0.1 mV s^{-1} ; (b) initial three galvanostatic charging/discharging curves of MPIT at 100 mA g^{-1} ; (c) rate capability tests; (e) cycle performance at 1 A g^{-1} ; (d) initial 100 cycles; (f) EIS tests at open circuit voltage.

superior electronic conductivity. The resistance reduced for MPI with smaller particle size, while it slightly increased after titania introduction.

In Figure 4, CV curves recorded at a series of scan rate are presented to distinguish the capacitive and diffusion-controlled contribution ratio based on Equation (1) (i represents the current while a and b are variables). The b -value could be derived from the slope of $\log i$ versus $\log$

v . When b -value approaches 0.5, the diffusion process is dominated, otherwise capacitive process controlled if the b -value is close to 1.0. The numerical values for cathodic and anodic peaks are 0.82 and 0.65 respectively, indicating a surface capacitive-dominated process. Figure 4(d) exhibits the comparison of capacitive current with the whole current measured. The pseudo-capacitance contributions at sweeping rates of 0.1, 0.3, 0.5, 0.7 and 0.9 mV

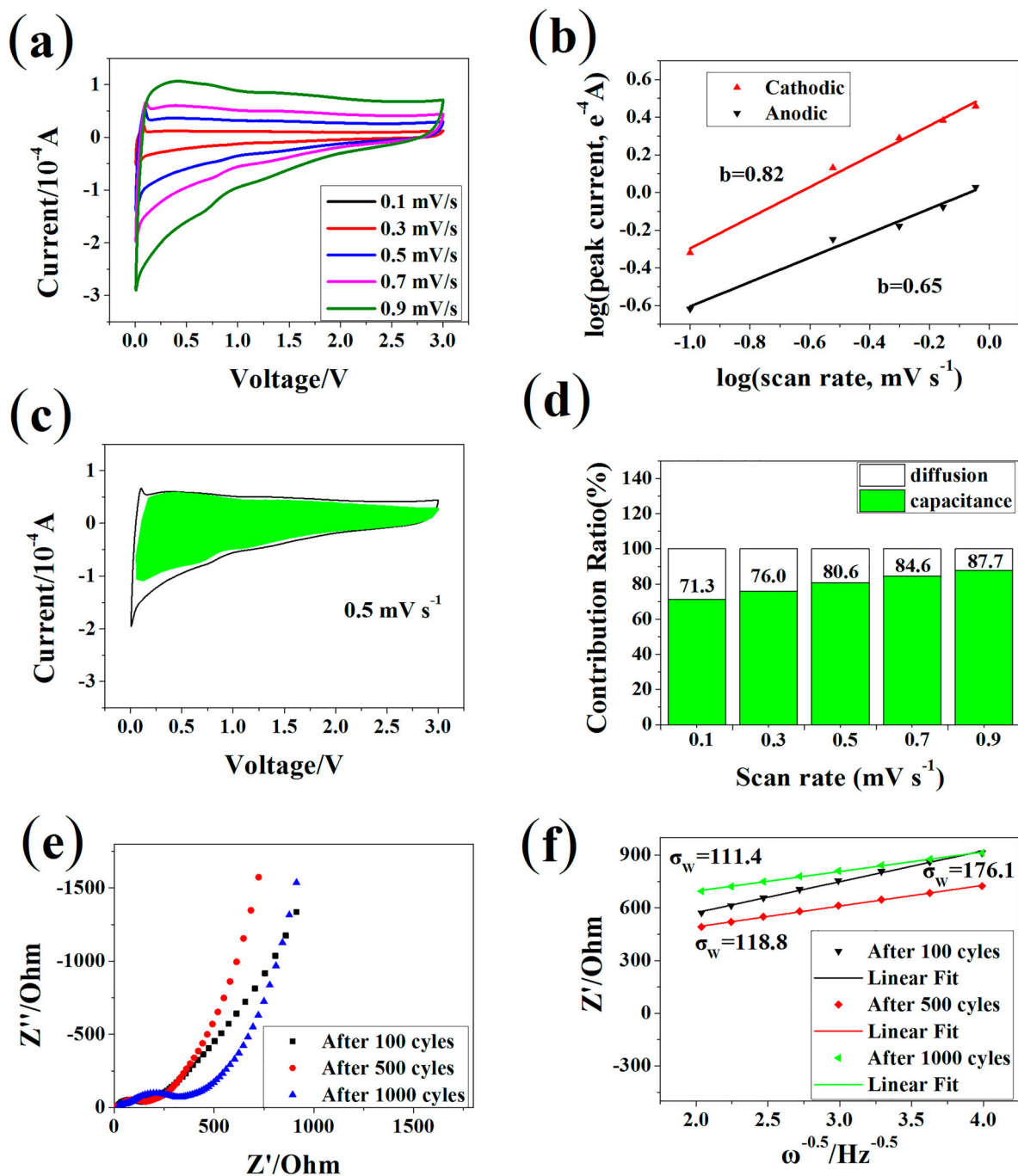


Figure 4. Electrochemical process kinetics analysis for MPIT. (a) CV curves at various sweeping rates from 0.1 to 0.9 mV s⁻¹, (b) corresponding log i versus log v , (c) CV curve with pseudo-capacitance contribution shown by the shaded area at 0.5 mV s⁻¹, (d) bar chart showing the capacitance percentage at different sweep rates, (e) EIS patterns collected after 100, 500, 1000 cycles and (f) corresponding relationship between Z'' and $\omega^{-1/2}$ for MPIT, the slope equals the Warburg coefficient (σ_w).

s⁻¹ are 71.3%, 76.0%, 80.6%, 84.6% and 87.7%, respectively.

$$i = av^b \quad (1)$$

$$i(v) = k_1 v + k_2 v^{1/2} \quad (2)$$

The EIS tests were performed at different cycling stage to study the electrochemical dynamics property of MPIT

sample. All the Nyquist spectra in Figure 4(e) can be divided into a semicircle in the high-medium frequent and a sloping line in the low frequency. The semicircle related to the charge transfer resistance tended to accumulate with cycles. Fitting the low frequency part from Equation (3), we can get the sodium ion diffusion factor related Warburg coefficient (σ_w), which declined upon initial charging/discharging and remained

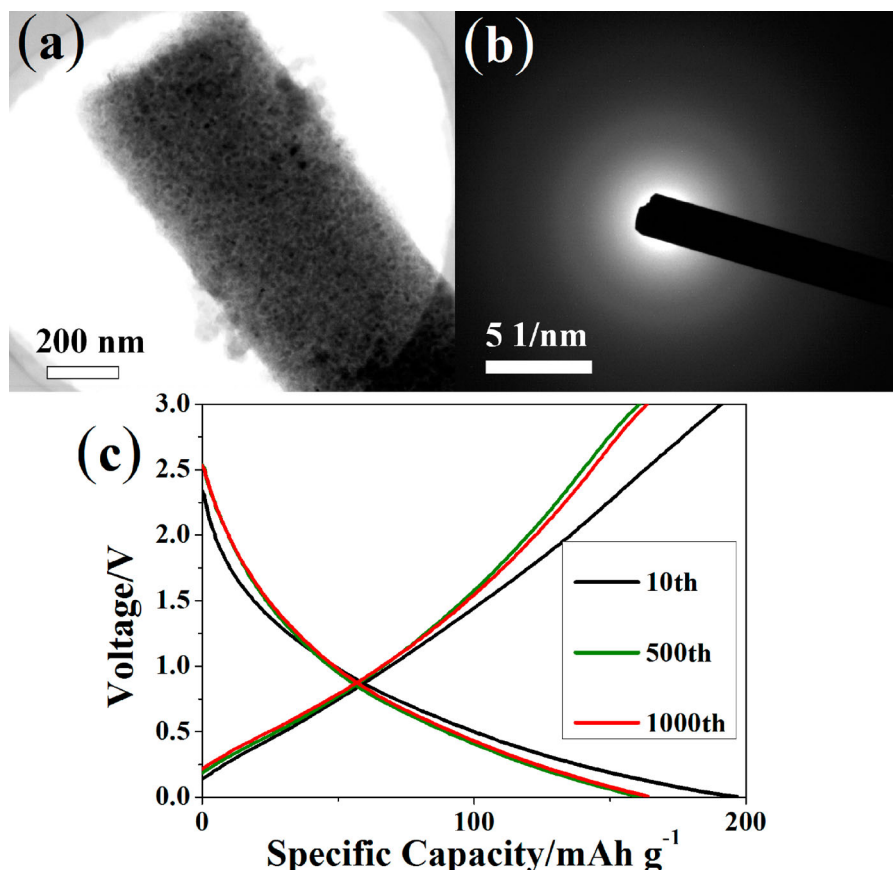


Figure 5. (a) TEM photos for expired electrode of MPIT, (b) SAED patterns and (c) representative charging-discharging curves at 1 A g^{-1} .

relatively stable in the subsequent cycles, implying improved diffusion property sustained by carbon fibers confined MoP/TiO₂ composite.

$$Z' = R_e + R_{ct} + \sigma_w \cdot \omega^{-1/2} \quad (3)$$

$$D_{Na^+} = R^2 T^2 / (2A^2 n^4 c_{Na^+}^2 \sigma_w^2) \quad (4)$$

To probe the underlying mechanisms behind the superior cycling durability of MoP/TiO₂, the expired electrodes were disassembled for TEM tests. As shown in Figure S6a, the cycled MP sample apparently experienced cracking and pulverization of particles, while the MPI and MPIT specimens almost retained its original morphology, illustrating the smaller particle size can effectively alleviate the stress brought by the volume variations upon cycling. Besides, the selected area electron diffraction (SAED) results (Figure 5b) confirmed that the active materials also went through an amorphization process, only weak signals can still be detected for the MP (Figure S6b). Due to the interfacial charge transfer promotion of MoP/TiO₂ heterostructure, buffering effect of TiO₂ and overpotential reducing effect of amorphization [27–29], the polarization during 1 A g^{-1} cycling

was reduced compared to MP and MPI (Figure S6e–6f). Therefore, it's significant to construct ultrasmall particles confined in nanofibers with heterostructure for the long-term durability.

Conclusion

Through electrospinning method with continuous heat treatment, the MoP nanocrystals encapsulated nanofibers were prepared and studied. The addition of aniline and the *in-situ* formed PMo₁₂-PANI helped to construct carbon matrix confined well-dispersed nanoparticles. The introduction of titania further enhanced the structure stability and greatly alleviated the stress upon cycling. CV and EIS tests proved the enhanced sodium ion storage reaction dynamics. The *ex-situ* TEM tests combined with charging–discharging curves illustrated the improvement for the interfacial charge transfer of titania. In a word, this work provides a convenient method for the construction of phosphide/carbon composites with stable performance. More detailed works can be explored for the further improvement of materials performance.

Impact statement

This work provides a simple and continuous way to fabricate nanofibers confined phosphide nanoparticles from electrospinning method, the as-prepared composites exhibit enhanced electrochemical performance as sodium ion battery anode.

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Disclosure statement

No potential conflict of interest was reported by the author(s).

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