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Supporting Information

An "inverted load" strategy to fabricate interface-optimized flexible electrode with superior electrochemical performance and ultrastability

*Ying Sun, Ying Yang, Ning-Bo Li, Meng Wang, Xu-Man Chen, Shuai Huang and Hong Yang**

School of Chemistry and Chemical Engineering, Jiangsu Province Hi-Tech Key Laboratory for Bio-medical Research, Jiangsu Key Laboratory for Science and Application of Molecular Ferroelectrics, Southeast University, Nanjing, Jiangsu Province 211189, China

E-mail: yangh@seu.edu.cn

Experiments

Fabrication of $W_{0.71}Mo_{0.29}O_3$/PEDOT:PSS/AgNWs/CPI (WPAC) Electrode

All reagents used were analytical grade and used without additional purification. The glass substrates with a dimension of 2 × 2 cm^2 were cleaned sequentially with detergent, deionized (DI) water, acetone, and isopropyl alcohol. $W_{0.71}Mo_{0.29}O_3$ ink was prepared according to the method previously reported by Li et al.[1] As shown in Fig. S1, the phase purity and crystal structure in the XRD are consistent with the previous work, all peaks match the monoclinic phase of $W_{0.71}Mo_{0.29}O_3$ (JCPDS No. 01-076-1279), which proves the successful preparation. A 7 mL diluted $W_{0.71}Mo_{0.29}O_3$ ink (conc. = 0.5 mg/mL) was sprayed uniformly with a spray gun onto a glass substrate placed on a 160 °C hot plate and the ink could be dried and oxidized immediately. In the next step, PEDOT:PSS (Clevios PH 1000, Heraeus) solution was mixed with 6 vol% methanol and 0.05 vol% Zonyl fluorosurfactant (FS-30, Dupont), and sonicated for 30 minutes at room temperature. A 700 μL modified PEDOT:PSS solution was then spin-coated onto the $W_{0.71}Mo_{0.29}O_3$/glass substrate at 2500 rpm for 100 s and dried at 110 °C on a hot plate for 10 min to form the PEDOT:PSS film. Afterwards, the acid treatment was carried out by dropping 8M CH_4SO_3 (MSA) aqueous solution on a PEDOT:PSS film and heated for 3 minutes at 150 °C on a hot plate, followed by immersing in DI water for three times and drying at 150 °C to remove residues. In the subsequent step, large aspect ratio AgNWs (L70, Nanjing Xianfeng Nano Co., Ltd.) was diluted in ethanol to prepare 1.0 mg/mL AgNWs dispersion. 500 μL AgNWs dispersion was then coated on the surface of PEDOT:PSS

film by spin-coating at 2500 rpm for 100 s and annealed at 80 °C for 20 min. Moreover, a polyamide acid (PAA) solution was prepared by the reaction of 2,2'-bis(trifluoromethyl)benzidine and 4,4'-(hexafluoroisopropylidene)diphthalic anhydride and incorporating 8 wt% ionic liquid 1-ethyl-3-methylimidazolium bis((trifluoromethyl)sulfonyl)imide to form a mixture of precursor according to the method described in the previous work.[2] 1.0 mL PAA solution was coated uniformly on the above AgNWs/PEDOT:PSS/$W_{0.71}Mo_{0.29}O_3$/glass substrate by a doctor blade. Subsequently, PAA solution was thermally imidized to form the thin CPI film by heat treatment, which was performed at 80 °C for 2 h, 110 °C for 2 h, 150 °C for 2 h, 170 °C for 2 h, 190 °C for 1 h, respectively. Finally, the composite film WPAC was peeled off from the glass substrate.

Fabrication of PEN/ITO/PEDOT:PSS/$W_{0.71}Mo_{0.29}O_3$ (PIPW) Electrode

Conducting transparent PEN/ITO substrates (6 Ω/sq, Shenzhen South China Xiangcheng Technology Co., Ltd) were cut into 2 × 2 cm^2 size. Before using, the plastic substrates were cleaned by a successive rinsing in acetone, ethanol, and DI water for 5 min and then dried under a gentle stream of nitrogen. A 700 μL modified PEDOT:PSS solution was then spin-coated onto the $W_{0.71}Mo_{0.29}O_3$/glass substrate at 2500 rpm for 100 s and dried at 110 °C on a hot plate for 10 min to form the PEDOT:PSS film. Afterwards, the acid treatment was carried out by dropping 8M CH_4SO_3 (MSA) aqueous solution on a PEDOT:PSS film and heated for 3 minutes at 130 °C on a hot plate, followed by immersing in DI water for three times and drying at 130 °C to remove residues. Afterwards, a 7 mL diluted $W_{0.71}Mo_{0.29}O_3$ ink (conc. =

0.5 mg/mL) was sprayed uniformly with a spray gun on PEN/ITO/PEDOT:PSS film placed on a 130 ° C hot plate and the ink could be dried and oxidized immediately.

Fabrication of CPI/AgNWs/PEDOT:PSS/$W_{0.71}Mo_{0.29}O_3$ (CAPW) Electrode

The glass substrates with a dimension of 2 × 2 cm^2 were cleaned sequentially with detergent, deionized (DI) water, acetone, and isopropyl alcohol. 500 μL AgNWs dispersion (conc. = 1.0 mg/mL) was then coated on the surface of glass substrates by spin-coating at 2500 rpm for 100 s and annealed at 80 °C for 20 min. Moreover, 1.0 mL PAA solution was coated uniformly on the above AgNWs/glass substrate by a doctor blade. Subsequently, PAA solution was thermally imidized to form the thin CPI film by heat treatment, which was performed at 80 °C for 2 h, 110 °C for 2 h, 150 °C for 2 h, 170 °C for 2 h, 190 °C for 1 h, respectively. After peeling off the AgNWs/CPI film, a 700 μL modified PEDOT:PSS solution was then spin-coated onto the AgNWs/CPI film at 2500 rpm for 100 s and dried at 110 °C on a hot plate for 10 min to form the PEDOT:PSS film. Afterwards, a 7 mL diluted $W_{0.71}Mo_{0.29}O_3$ ink (conc. = 0.5 mg/mL) was sprayed uniformly with a spray gun on CPI/AgNWs/PEDOT:PSS film placed on a 130 ° C hot plate and the ink could be dried and oxidized immediately.

Fabrication of PEN/ITO/$W_{0.71}Mo_{0.29}O_3$ (PIW) Electrode

Conducting transparent PEN/ITO substrates (6 Ω/sq, Shenzhen South China Xiangcheng Technology Co., Ltd) were cut into 2 × 2 cm^2 size. Before using, the plastic substrates were cleaned by a successive rinsing in acetone, ethanol, and DI water for 5 min and then dried under a gentle stream of nitrogen. Afterwards, a 7 mL

diluted $W_{0.71}Mo_{0.29}O_3$ ink (conc. = 0.5 mg/mL) was sprayed uniformly with a spray gun on PEN/ITO substrate placed on a 130 ° C hot plate and the ink could be dried and oxidized immediately.

Characterization

The phase structures of samples were characterized by using X-ray diffraction (XRD, Ultima IV, Rigaku Corporation, Japan). The Electrical conductivity of the composite films were measured by the four-probe tester (RTS-9, Guangzhou four-probe Technology Co., Ltd, China). The morphology of composite films were characterized by field-emission scanning electron microscopy (FE-SEM, Ultra Plus, Zeiss, Germany). The surface roughness of composite films were characterized by atomic force microscopy (AFM, Dimension ICON, Bruker, Germany). The optical performance of the composite films were measured by ultraviolet spectrometer (UV-2450, Shimadzu, Japan).The mechanical properties of the films were characterized by a electronic universal testing machine (E42.503, SANS). The electrochemical performance of electrodes were characterized by an electrochemical workstation (CHI660, Chenhua, Shanghai) for cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS).

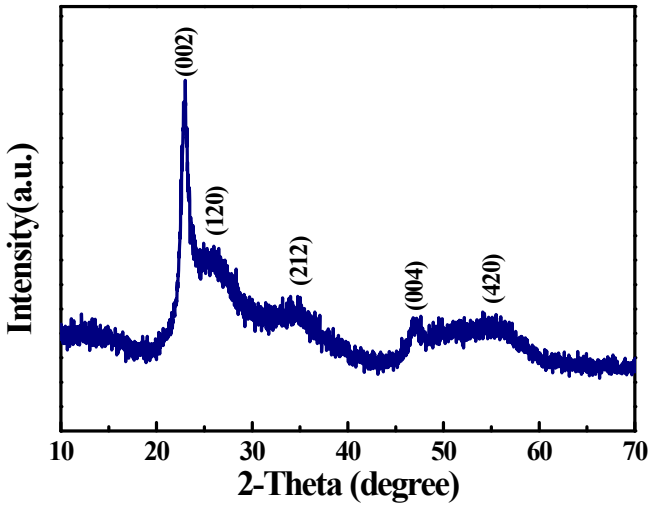

Fig. S1. XRD spectrum of prepared $W_{0.71}Mo_{0.29}O_3$ ink.

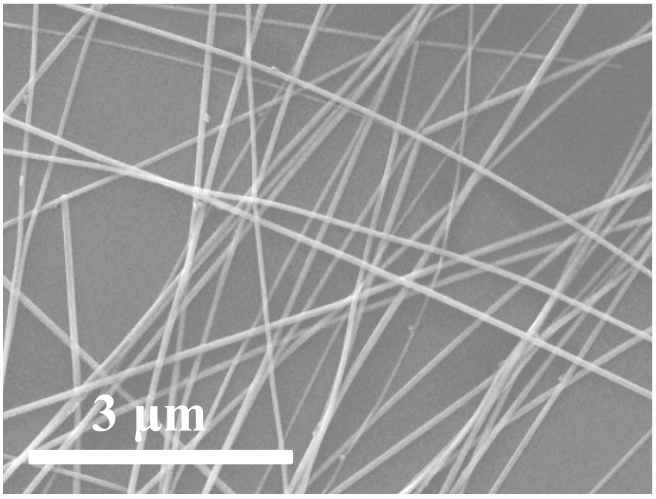

Fig. S2. FE-SEM photograph of the spin-coated, interconnected AgNWs network.

Tab. S1. Properties of CPI composite films.

Properties	Value
Film thickness (μm)	23.0
transmittance at 450 nm (%)	90.4
Thermal decomposition temperature at 5% weight loss (℃)	401.0
Tensile strength (MPa)	48.2
Tensile modulus (MPa)	844.6
Elongation at break (%)	108.4

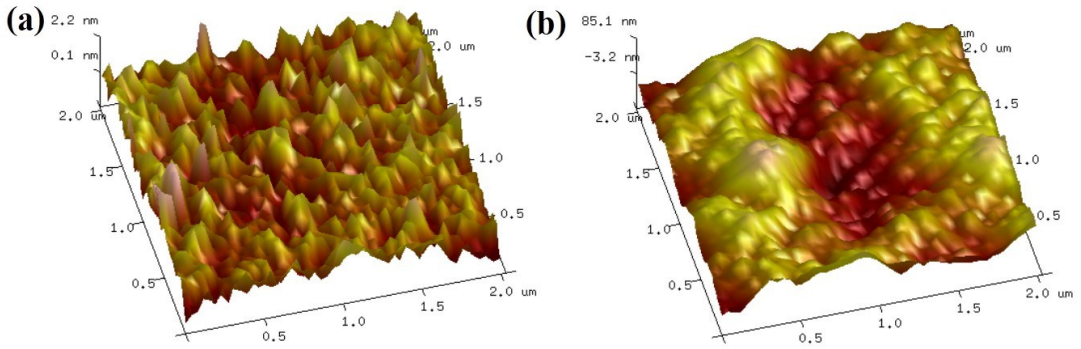

Fig. S3. AFM images of $W_{0.71}Mo_{0.29}O_3$ side on (a) WPAC and (b) PIPW, respectively.

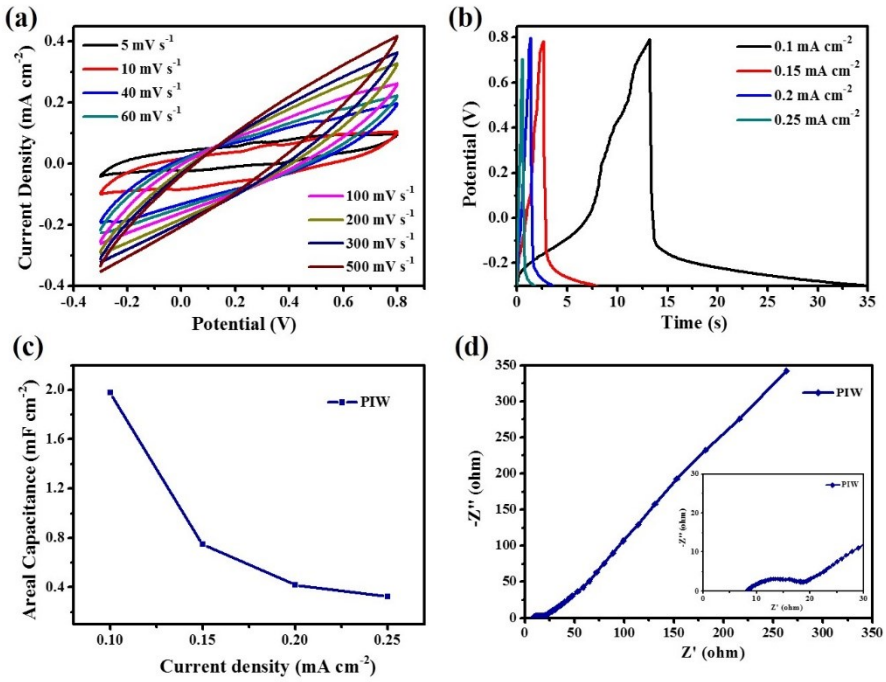

Fig. S4. (a) Cyclic voltammograms and (b) galvanostatic charge/discharge curves of PIW electrode. (c) Areal capacitance of PIW electrode at various current densities. (d) Nyquist plot of PIW electrode, the inset show the corresponding magnified Nyquist plots in high-frequency region.

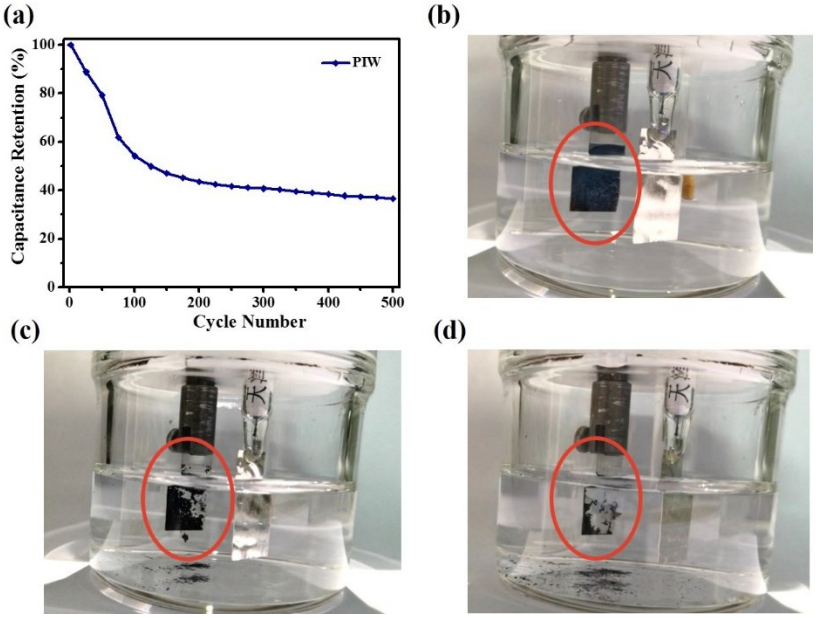

Fig. S5. (a) Cyclic stability performance of PIW electrode under 500 repeated CVs at scan rate of 100 mV s^{-1}. (b), (c), (d) Digital photos of active material $W_{0.71}Mo_{0.29}O_3$ loaded on PIW electrode that gradually sheds as the CV cycle progresses.

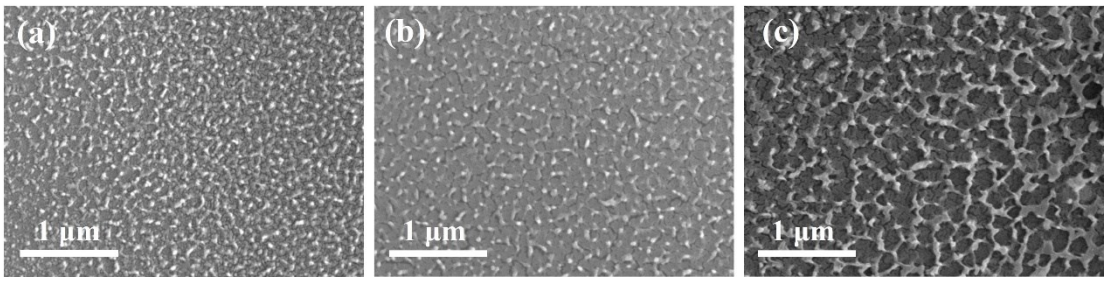

Fig. S6. The FE-SEM photograph of the WPAC electrode (a) before and after (b) 1000, (c) 3000 CV cycles at a scan rate of 100 mV s^{-1}.

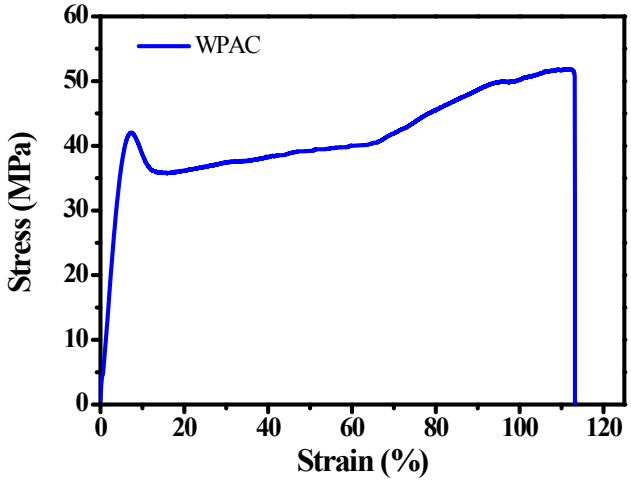

Fig. S7. Tensile stress-strain curves of WPAC composite films.

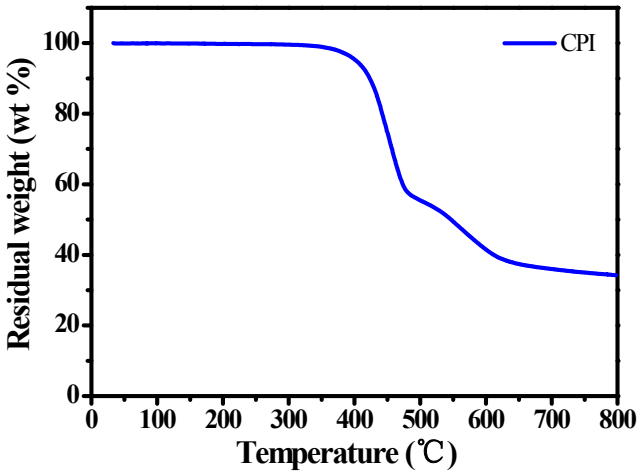

Fig. S8. Thermogravimetric analysis (TGA) curve of CPI film.

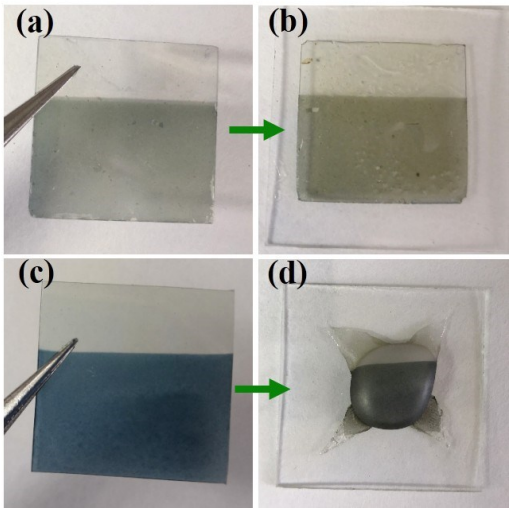

Fig. S9. Digital photo of WPAC electrode (a) before and (b) after 200 °C heat treatment for 5 minutes. Digital photo of PIPW electrode (c) before and (d) after 200 °C heat treatment for 1 minute.

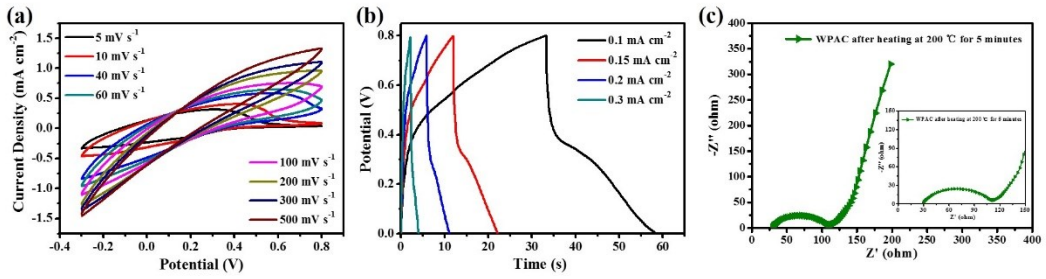

Fig. S10. (a) Cyclic voltammograms, (b) galvanostatic charge/discharge curves and (c) Nyquist plot of WPAC electrode after 200 °C heat treatment for 5 minutes.

References

1 H. Li, J. Li, C. Hou, D. Ho, Q. Zhang, Y. Li and H. Wang, *Adv. Mater. Technol.*, 2017, **2**, 1700047.

2 N. B. Li, M. Wang, L. X. Guo, B. P. Lin and H. Yang, *Polymer*, 2018, **153**, 538-547.