

Sulfidation-MnO₂ Dual-Modified Cu-Co-MOFs for Flexible Supercapacitors with Hydrogel Electrolyte

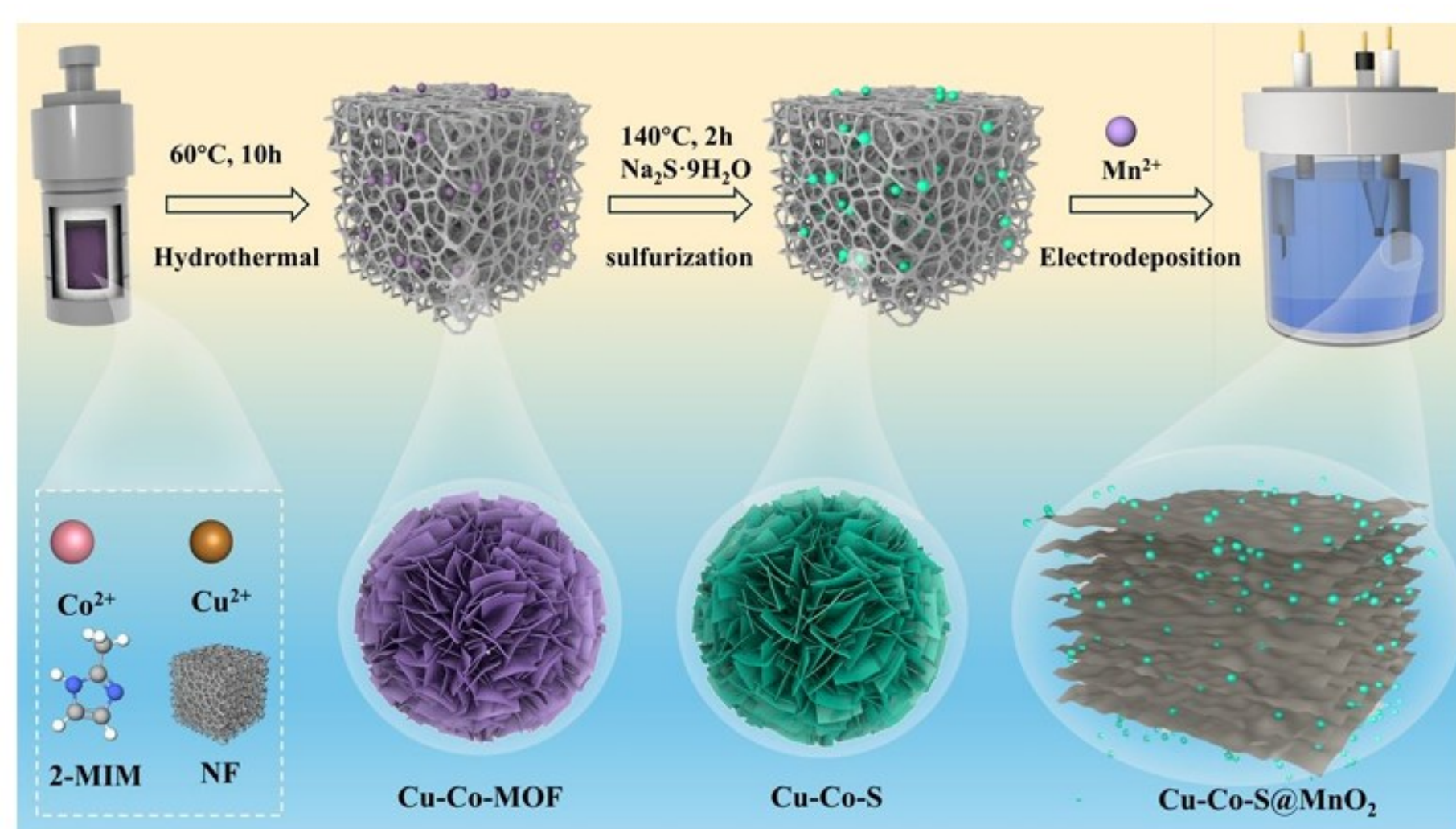
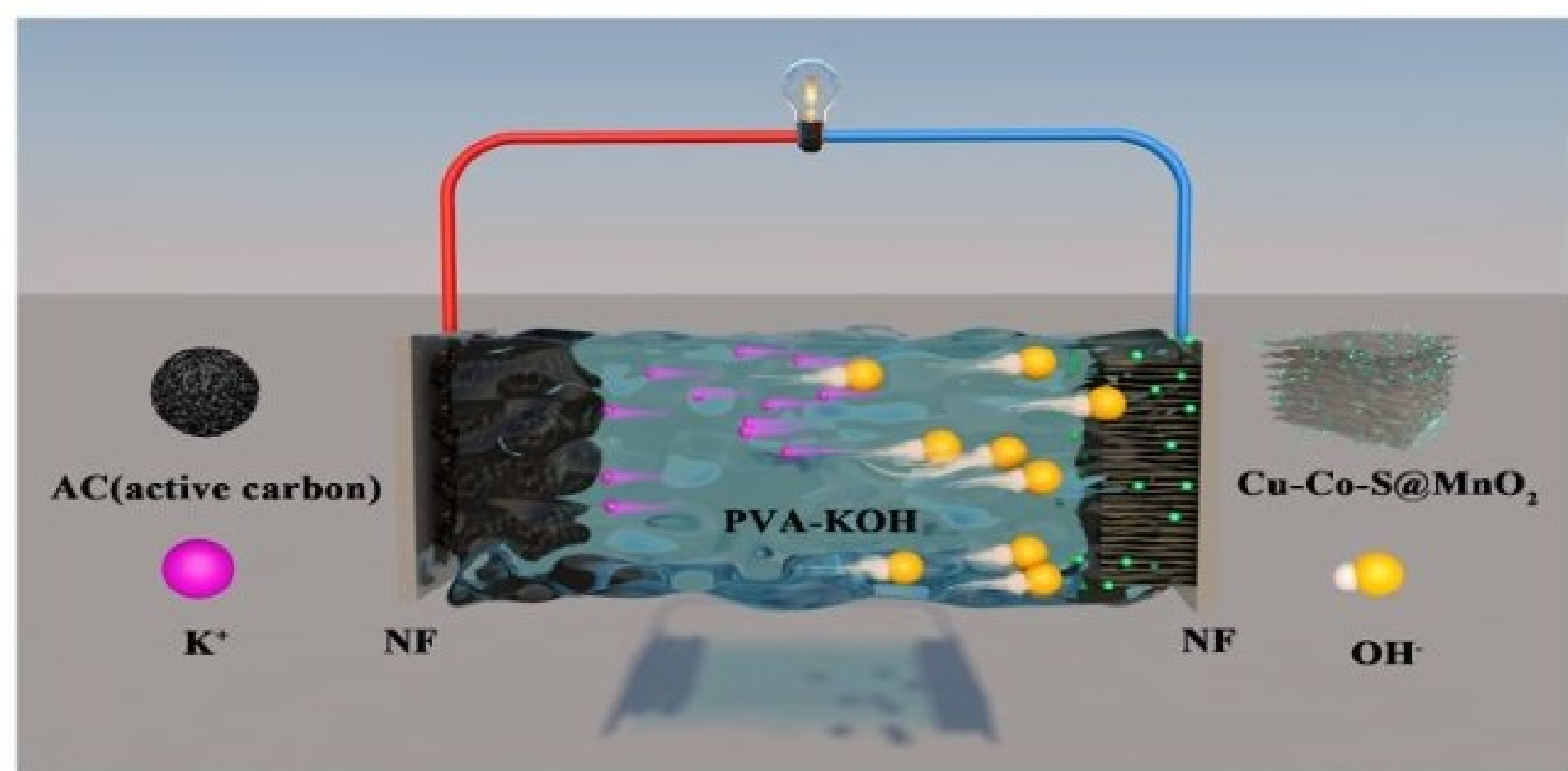
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INTRODUCTION & AIM

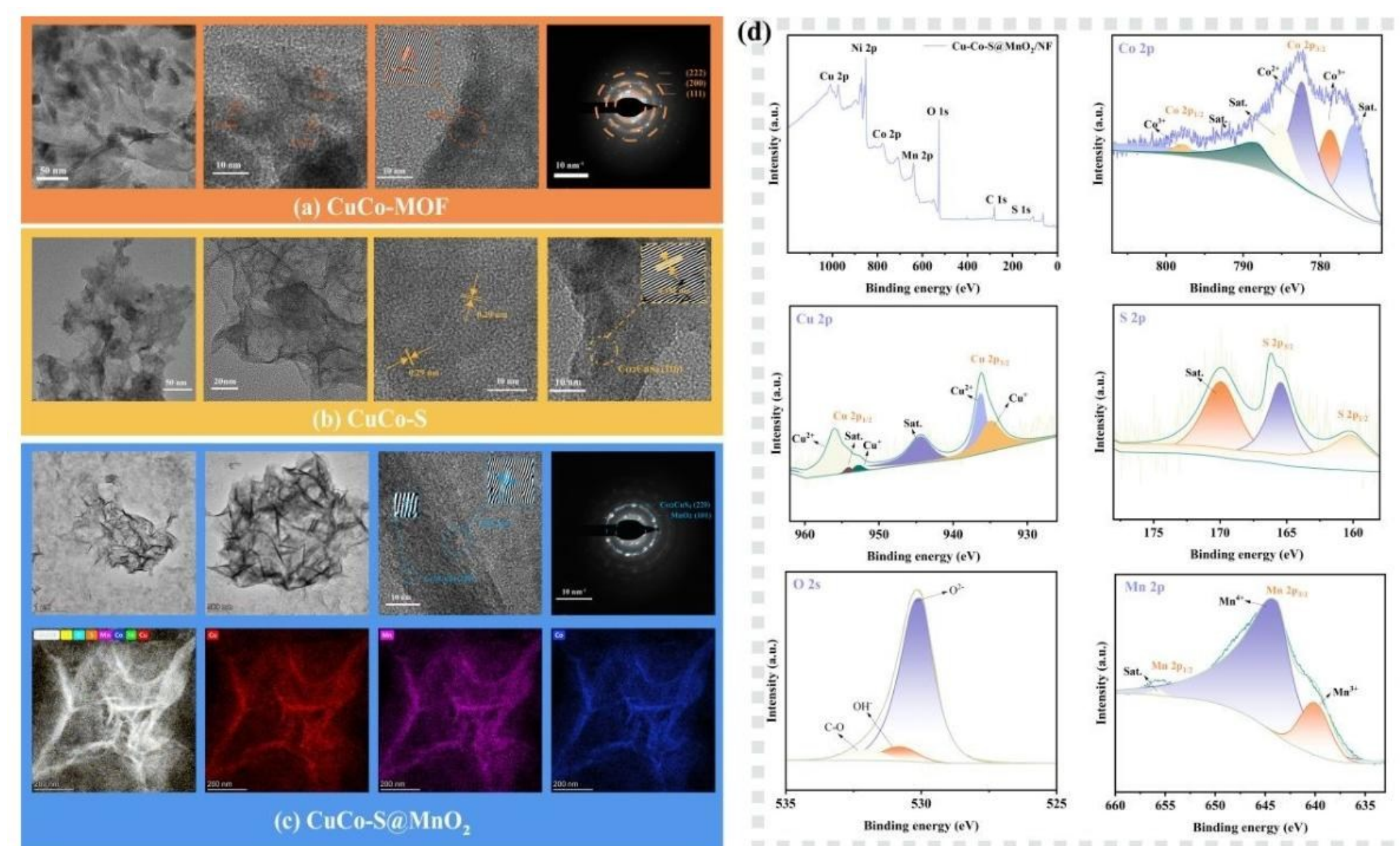
Metal-organic frameworks (MOFs) are promising advanced energy storage materials due to their high specific surface area and structural tailorability, but suffer from intrinsic poor conductivity and insufficient structural stability. This study proposes a dual-modification strategy combining controlled sulfidation and conformal MnO₂ coating. Bimetallic Cu-Co-MOFs were hydrothermally synthesized on nickel foam, then sulfided into Cu-Co-S (3.8-fold conductivity enhancement) with subsequent electrochemical deposition of MnO₂ to form hierarchical heterojunctions. The optimized Cu-Co-S@MnO₂ electrode delivers 1842 F g⁻¹ at 1 A g⁻¹ and 91.3% capacitance retention after 10,000 cycles. The flexible asymmetric supercapacitor achieves 68.4 Wh kg⁻¹ at 850 W kg⁻¹ and 88.7% retention over 15,000 bending cycles, validating the strategy for high-performance wearable electronics.

METHOD

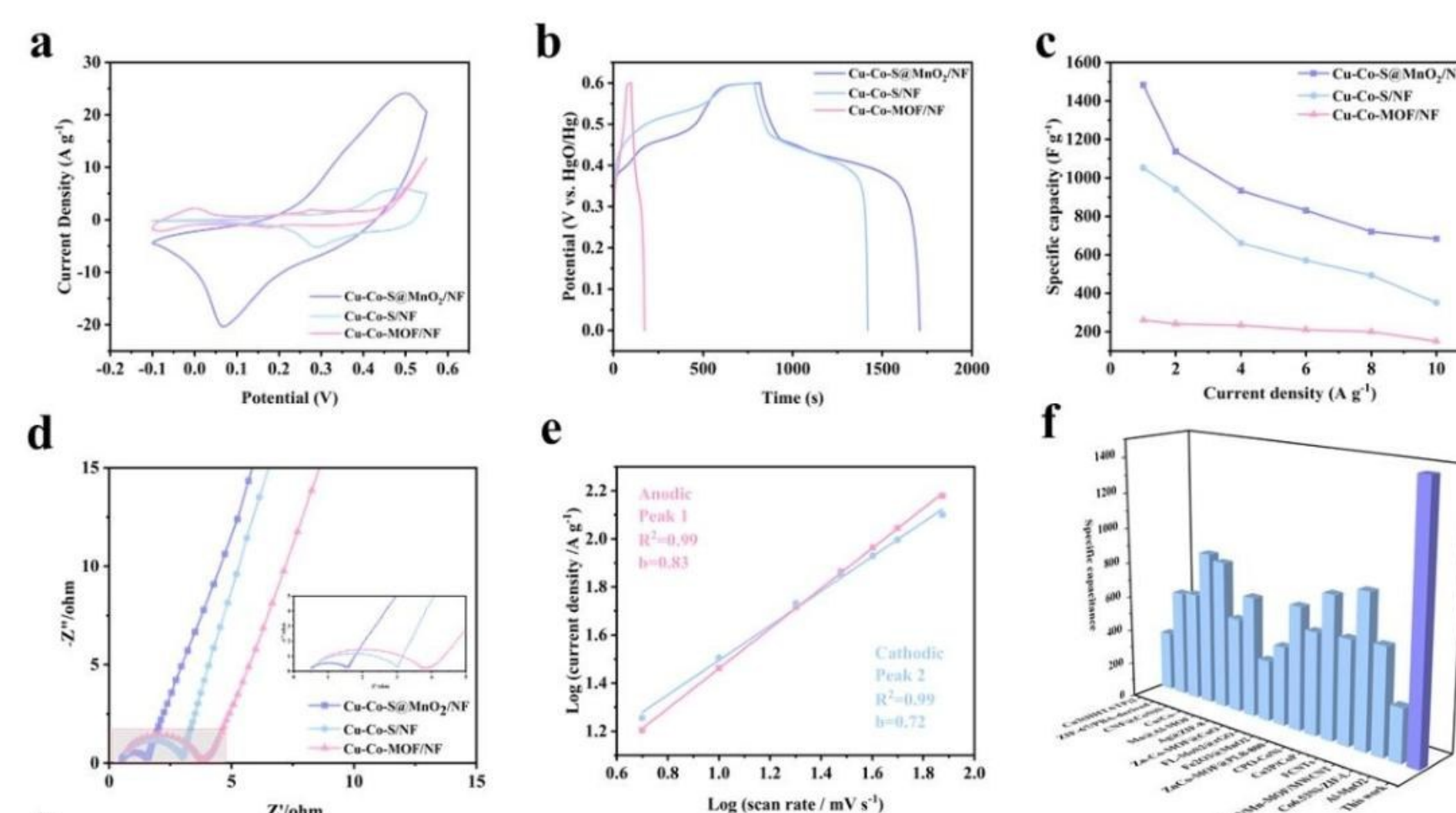
Schematic synthesis of Cu-Co-S@MnO₂Schematic diagram of the assembly of Cu-Co-S@MnO₂ flexible supercapacitor and the ion transport

- Dissolve polyvinyl alcohol (PVA) and potassium hydroxide (KOH) in water, heat and stir until fully dissolved to get a transparent mixture;
- After defoaming the mixture, pour it into a mold, and repeat freezing (-18~-20°C) and thawing (room temperature) 3-5 times to let PVA form a cross-linked network;
- Take it out and cut into shape to obtain KOH-PVA hydrogel.

RESULTS & DISCUSSION



TEM shows Cu-Co-MOF's flower-like shape, Cu-Co-S's clear lattice, and uniform MnO₂ coating forming heterojunctions, verifying structural design. XPS of Cu-Co-S@MnO₂ detects valence states (Mn⁴⁺/Mn³⁺, Cu²⁺/Cu⁺, Co²⁺/Co³⁺), confirming interfacial charge transfer.



In electrochemical tests, the Cu-Co-S@MnO₂ electrode has a specific capacitance of 1483.3 F g⁻¹ at 1 A g⁻¹, retaining 93% capacitance after 10,000 cycles. The flexible asymmetric device built with it achieves 185.25 Wh kg⁻¹ energy density at 0.75 kW kg⁻¹, with 88.1% capacitance retention after 5,000 cycles, showing excellent performance.

CONCLUSION

In the study, PVA-KOH hydrogel was used as the solid electrolyte for the flexible asymmetric supercapacitor. Prepared via the freeze-thaw method (mixing PVA and KOH aqueous solution followed by repeated freeze-thaw cross-linking), it not only endows the device with flexibility but also helps it retain 88.1% capacitance after 5,000 cycles, enhancing energy storage stability.

FUTURE WORK / REFERENCES

- ◆ Apply in-situ techniques (in-situ TEM/XPS) to observe Cu-Co-S@MnO₂ heterojunction evolution in real time, verifying the built-in electric field effect.
- ◆ Integrate the flexible supercapacitor with wearable devices, testing its stability under different temperatures/humidity.
- ◆ Add nanofillers (e.g., SiO₂, graphene) to PVA-KOH hydrogel to improve its ionic conductivity and mechanical strength.