

Covalent Organic Framework Derived-Heteroatoms Rich Porous Carbon/Polymer Composite Electrode for High-Performance Energy Storage Applications

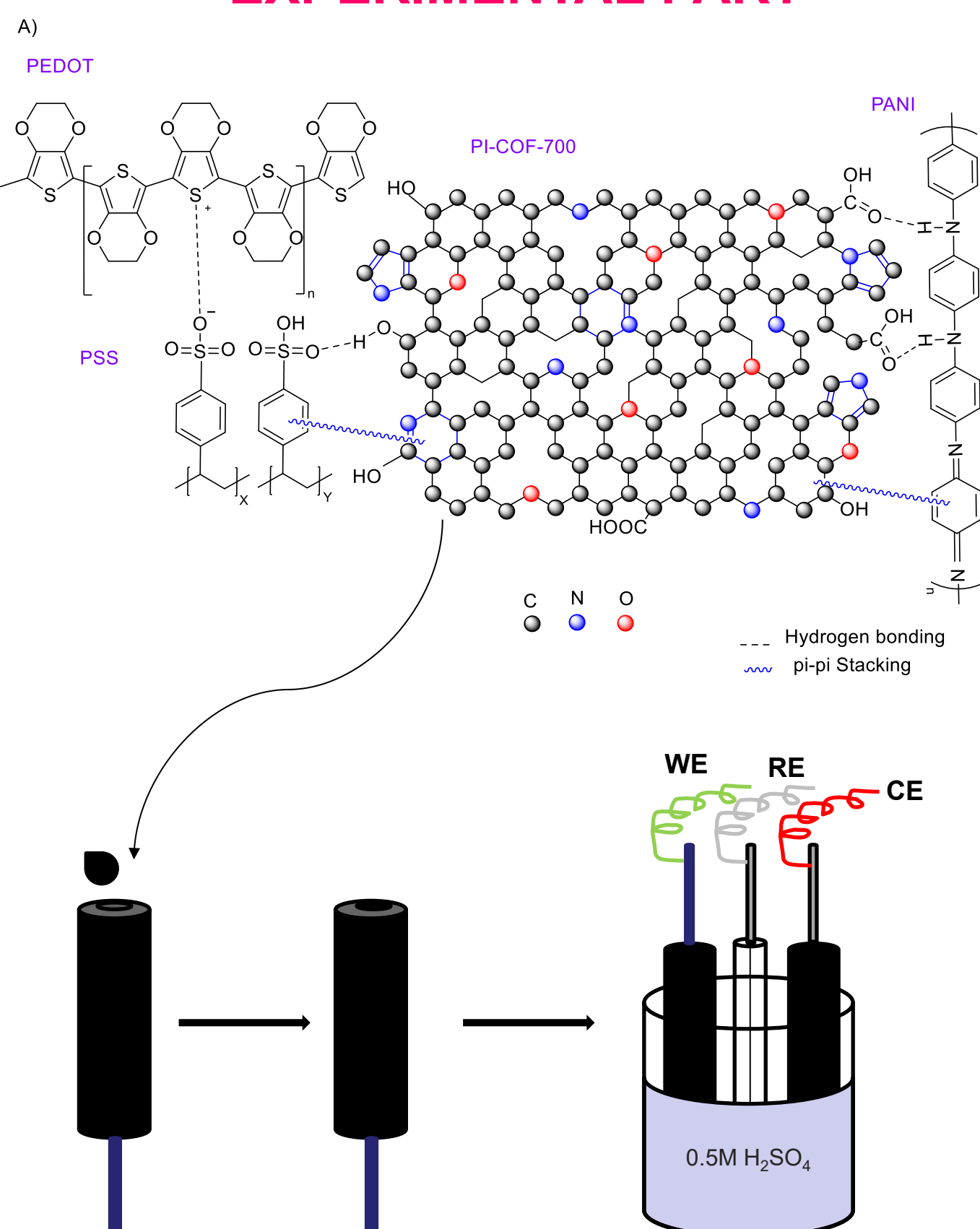
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ABSTRACT

Heteroatom-doped porous carbons are promising electrode materials for supercapacitors due to their high capacitance and favorable surface properties. Here, we report a nitrogen-rich porous carbon (PI-COF-700) derived from a polyimide covalent organic framework (PI-COF) synthesized via the condensation of 1,3,5-tris(4-aminophenyl) benzene and pyromellitic dianhydride under solvothermal conditions. The amorphous defective carbon nature and variation in functional groups of pyrolyzed PI-COF-700 were studied through physicochemical characterizations. In addition, the porous carbon presents a large surface area of 1080 m²g⁻¹ and a high micropore distribution ratio, which was observed from nitrogen adsorption/desorption isotherm measurement. Later, we developed a strategy of compositing PI-COF-700 with polyaniline (PANI) and poly(3,4-ethylenedioxythiophene)/poly(4-styrenesulfonate) (PEDOT/PSS) as an electrode material for supercapacitor application. The modified composite material exhibited a high specific capacitance value of 729.17 Fg⁻¹ at an applied current density of 2 Ag⁻¹, surpassing many of the previously reported supercapacitors based on organic framework-derived porous carbon composite systems. In addition, PANI/PEDOT/PSS@PI-COF-700 showed a capacitance retention close to ~92.2% after 1000 cycles at an applied current density of 20 Ag⁻¹. An aqueous electrolyte-based symmetric supercapacitor electrode system constructed with this material demonstrated a specific capacitance of ~182 Fg⁻¹ at 0.2 Ag⁻¹ and 89.81% retention after 10,000 cycles at 30 Ag⁻¹. Beyond supercapacitors, the tunable porosity, high conductivity, and heteroatom-rich framework of this COF-derived carbon suggest strong potential for cathode design and polysulfide confinement in lithium-sulfur and other metal-anode battery systems. Collectively, these findings highlight the broad applicability of COF-derived porous carbon/polymer composites as multifunctional electrode platforms for next-generation, high-performance, energy storage technologies.

Keywords: COF; pyrolysis; defective carbon; porous material; polymer composites; symmetric supercapacitors

EXPERIMENTAL PART



Surface Area and pore size

Sample	BET SA	Pore size distribution
PI-COF	335 m ² g ⁻¹	2.2 nm (mesoporous)
PI-COF-700	1080 m ² g ⁻¹	1 nm (microporous)

RESULTS and DISCUSSION

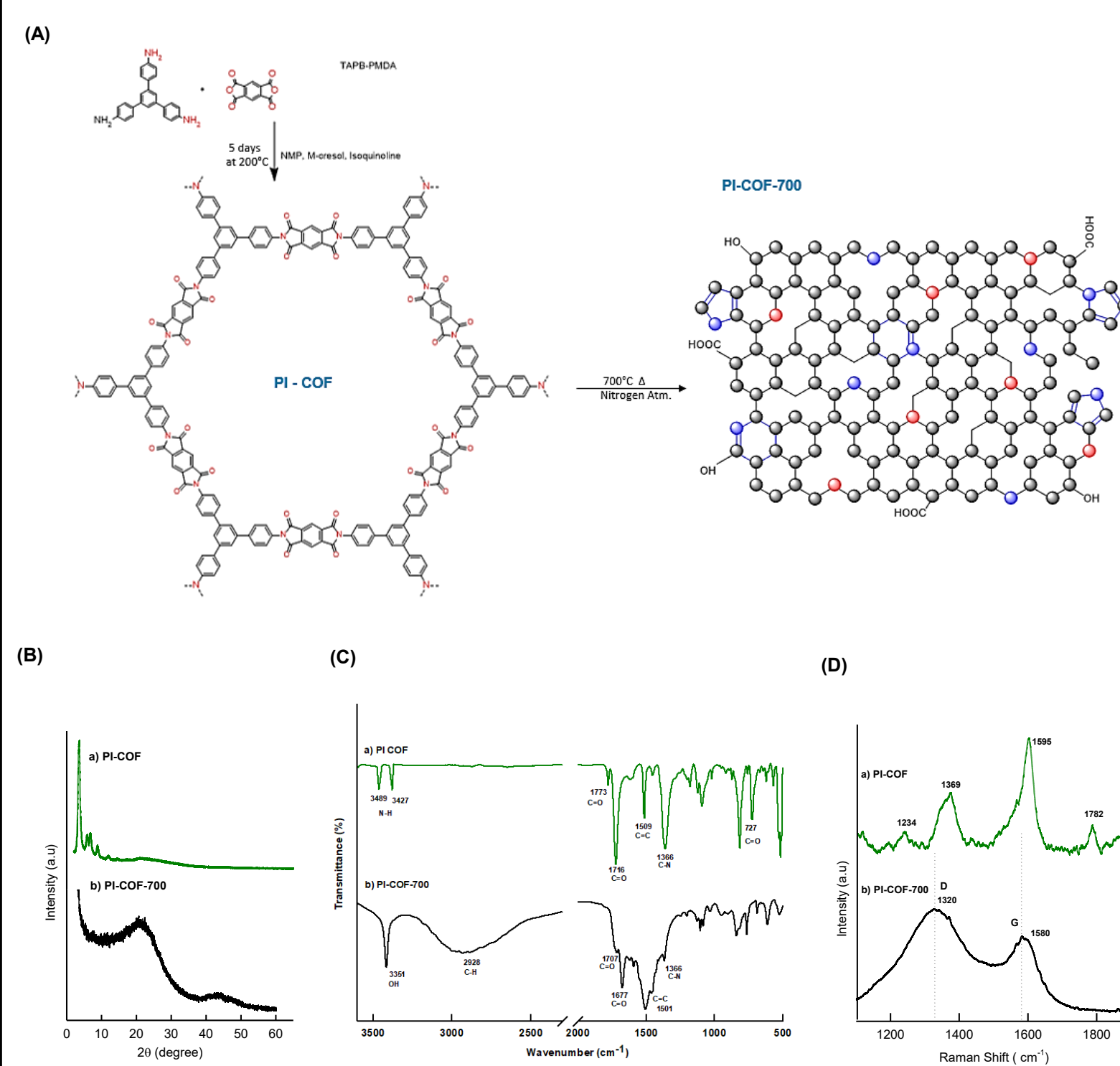


Figure 1. (A) Schematic illustration of PI-COF and PI-COF-700 synthesis protocols. Physicochemical characterizations of PI-COF and pyrolyzed PI-COF-700 by (B) XRD, (C) FTIR, and (D) Raman spectroscopy.

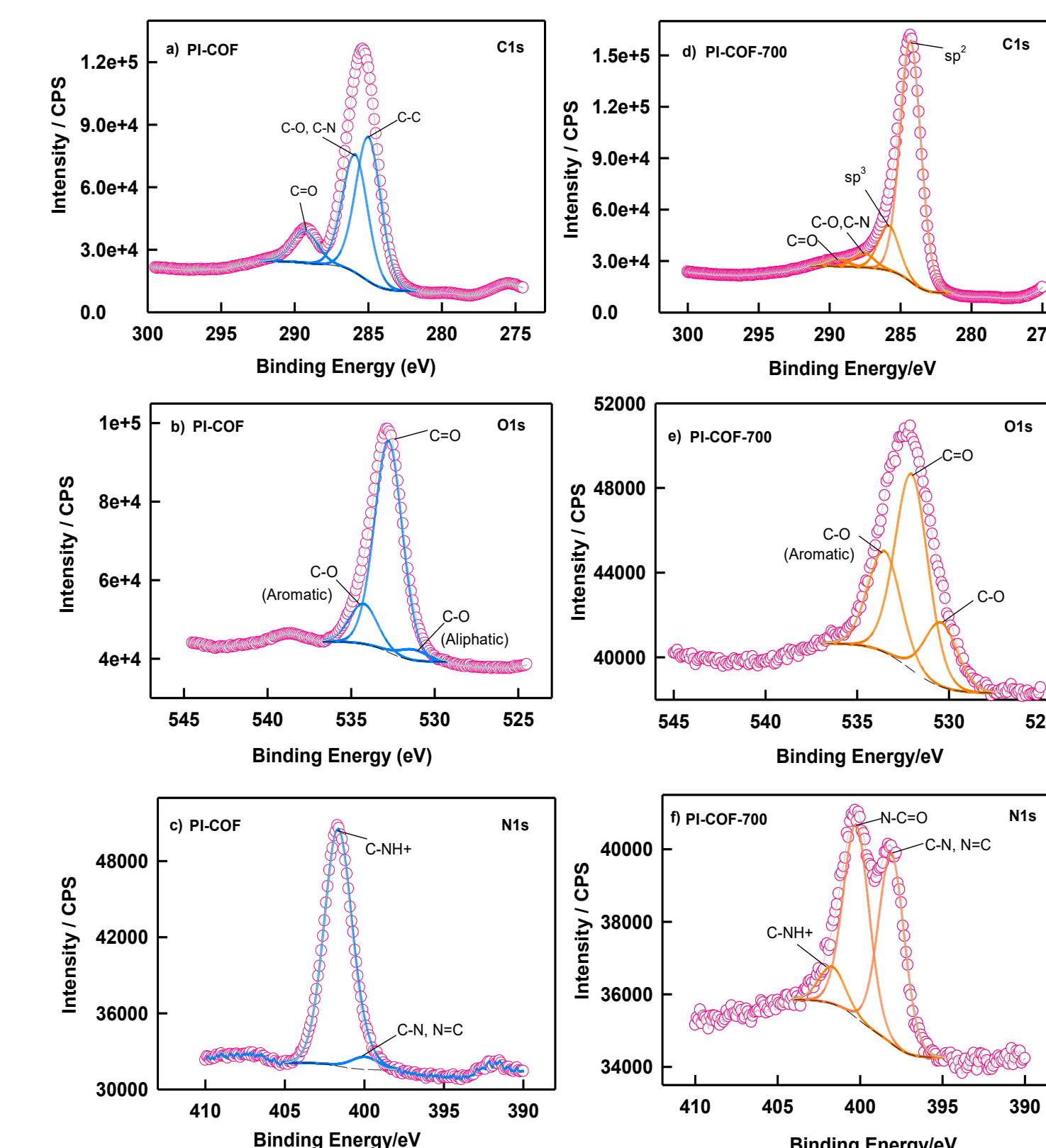
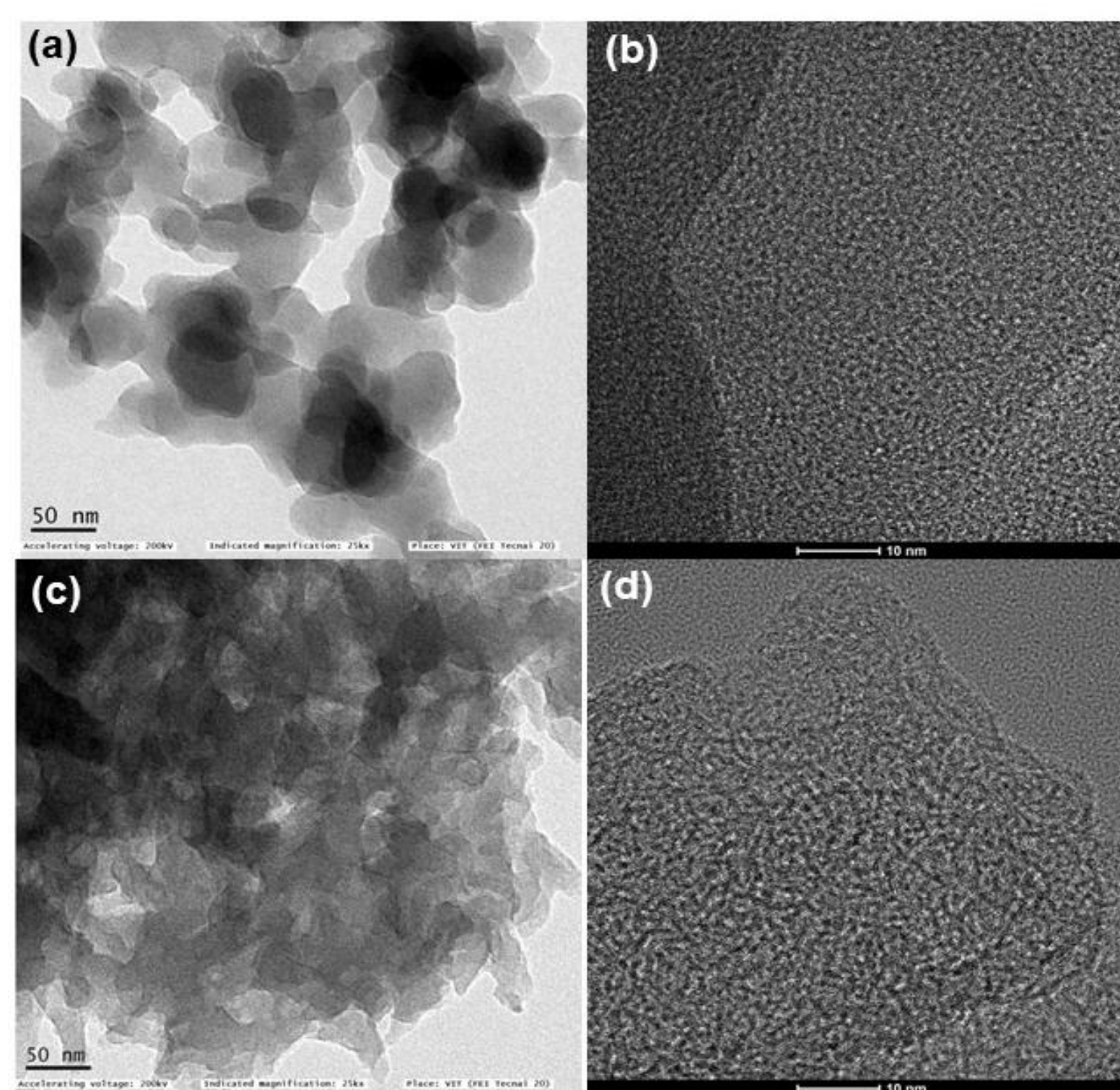


Figure 2. Transmission Electron Microscopy images of (a, b) PI-COF, (c, d) PI-COF-700 and XPS energy-level spectra of C1s, O1s, and N1s of (a-c) PI-COF and (d-f) PI-COF-700.

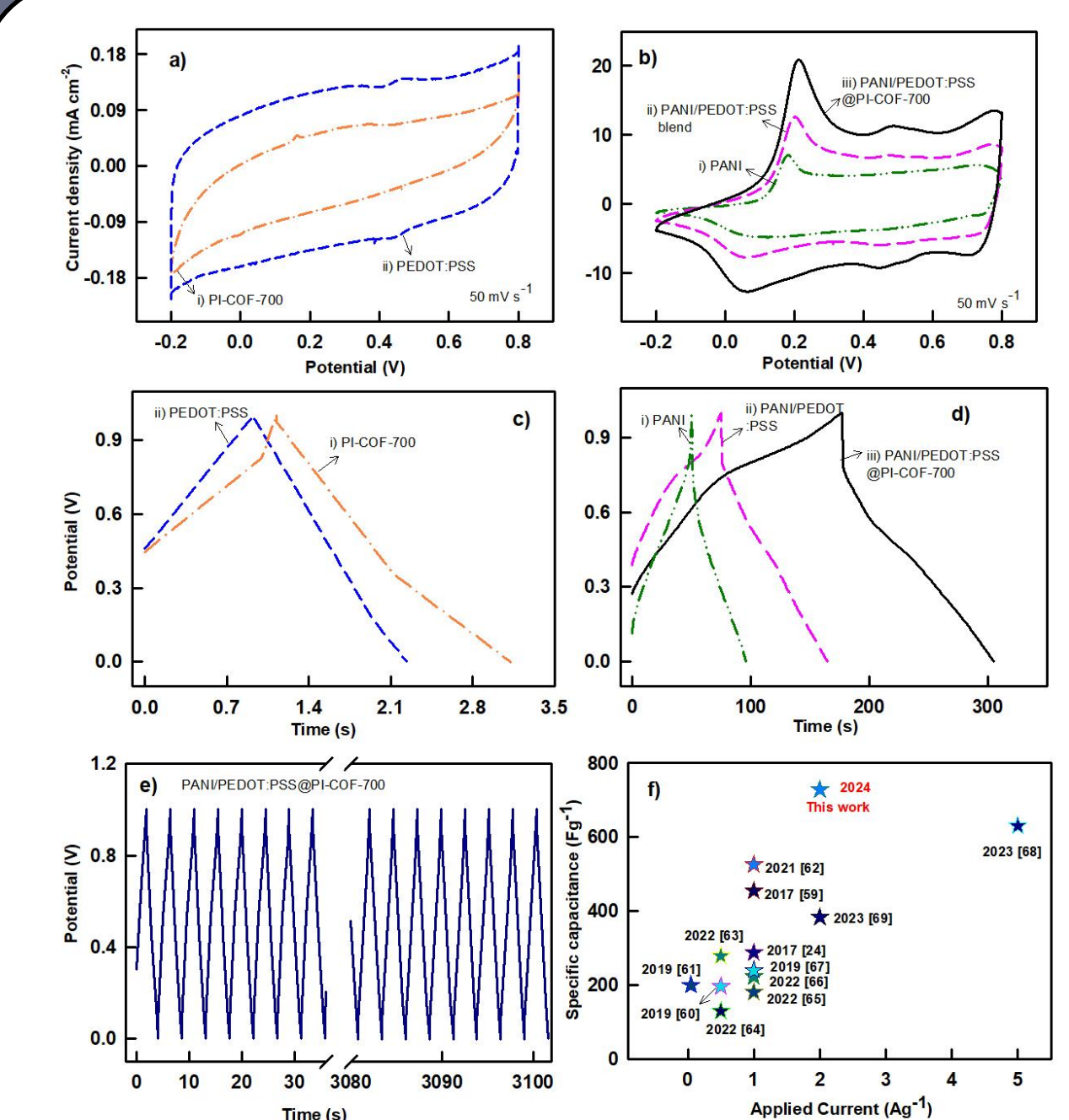


Figure 3. CV curves of (a) PI-COF-700 and (b) PANI, (c) PANI-PEDOT/PSS blend, and (d) PANI-PEDOT/PSS@PI-COF-700 in 0.5M H₂SO₄ solution at a scan rate of 50 mV s⁻¹. Galvanostatic charge/discharge response of (e) PI-COF-700 and (f) PEDOT/PSS and (d) PANI, (ii) PANI-PEDOT/PSS, and (iii) PANI-PEDOT/PSS@PI-COF-700 in 0.5M H₂SO₄ solution at an applied current density of 2 Ag⁻¹. (e) Continuous charge-discharge response of PANI-PEDOT/PSS@PI-COF-700 at an applied current density of 20 Ag⁻¹ for 1000 cycles. (f) Ragone plot of the PANI-PEDOT/PSS@PI-COF-700 composite's supercapacitance performance compared with different porous carbon-based literature reports.

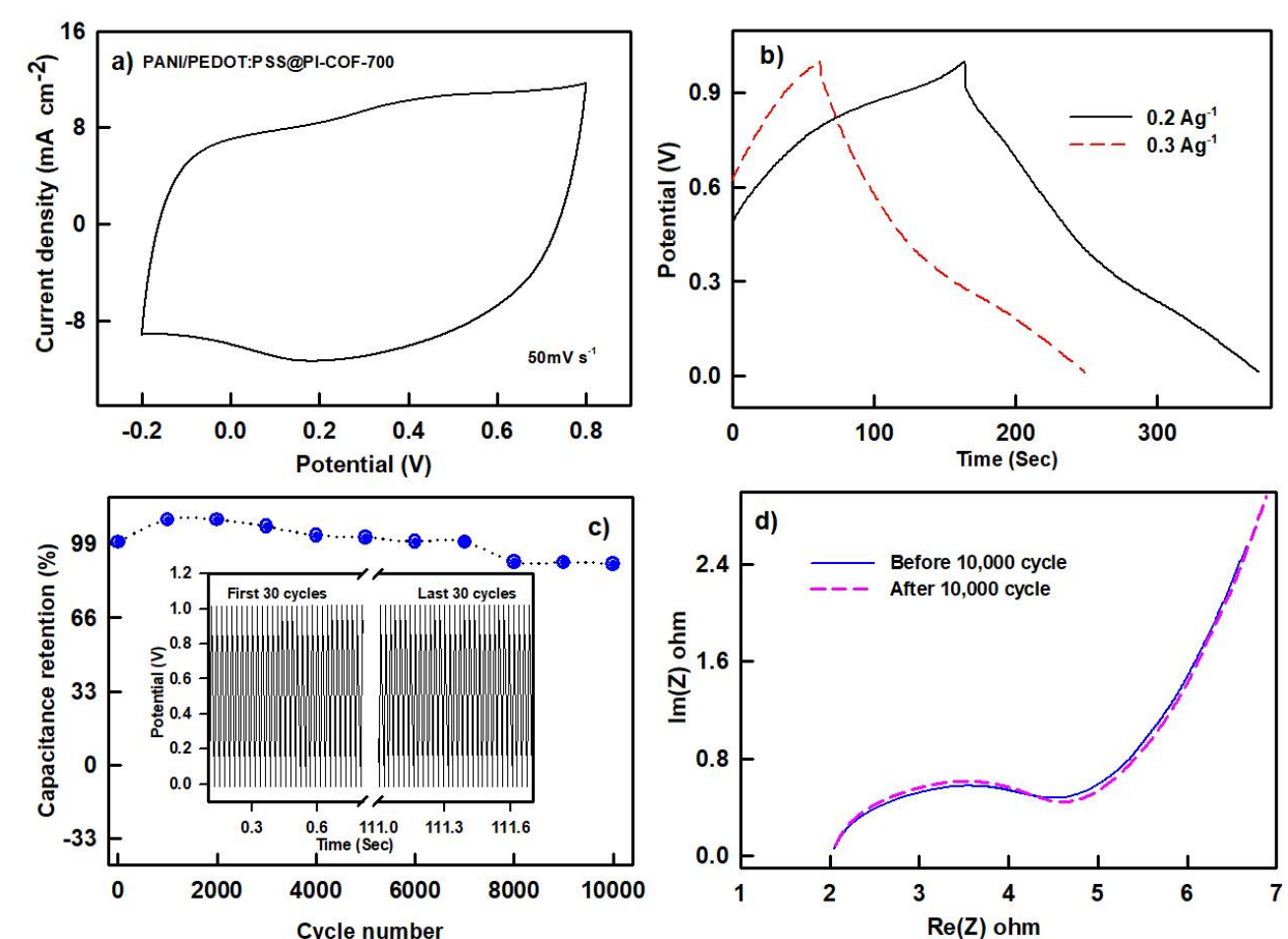


Figure 4. Performance of fabricated optimal PANI-PEDOT/PSS@PI-COF-700 composite electrodes as a symmetric supercapacitor system (SPE). (a) CV curve of PANI-PEDOT/PSS@PI-COF-700 in 0.5M H₂SO₄ solution at a scan rate of 50 mV s⁻¹. (b) Galvanostatic charge/discharge response of PANI-PEDOT/PSS@PI-COF-700 in 0.5M H₂SO₄ solution at an applied current density of 0.2 (black) and 0.3 (red) Ag⁻¹. (c) Continuous charge-discharge response of PANI-PEDOT/PSS@PI-COF-700 at an applied current density of 30 Ag⁻¹ for 10,000 cycles. (d) Nyquist plot of the PANI-PEDOT/PSS@PI-COF-700 composite before (blue) and after (pink) 10,000 cycles.

CONCLUSIONS

- **Successful Development of Porous Nitrogen-Doped Carbon (PI-COF-700):** A periodically ordered PI-COF precursor was synthesized and carbonized to form PI-COF-700. Carbonization induced a transition from mesoporous to microporous structure, increased surface area to 1080 m²/g, and induced nitrogen-linked defects.
- **Enhanced Structural and Electrochemical Properties:** The N-doped microporous carbon provided a more disordered structure with abundant active sites, improving conductivity, ion transport, and stability for electrochemical applications.
- **Superior Supercapacitor Performance in Composite System:** Incorporation of PI-COF-700 into a PANI/PEDOT/PSS matrix significantly improved impedance, reduced resistance (3.3 Ω), and delivered high specific capacitance (729.17 Fg⁻¹ at 2 Ag⁻¹), along with excellent rate capability and long-term cycling stability (92.2% retention after 1000 cycles; 89.81% after 10,000 cycles in symmetric device).
- **Robust Stability:** In an acidic environment, other carbon materials may corrode or degrade over prolonged cycling. In contrast, porous carbon derived from polyimide COF offers a stable chemical structure, tolerate high temperatures and can withstand harsh chemical conditions.
- **Application Potential:** High surface area, N-doping, and a stable carbon framework make PI-COF-derived porous carbon as an ideal source for durable high-performance energy storage application.

ACKNOWLEDGEMENTS

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