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Original Research

Polyaniline-Based Flexible Energy Storage Devices: Mechanisms, Progress, Optimization Strategies, and its Photo-enhanced Applications

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Abstract: With the rapid development of the flexible electronics industry, energy storage devices with excellent electrochemical performance and flexibility have become a research hot spot. Polyaniline (PANI) has become a core electrode material for flexible energy storage devices due to its advantages of abundant raw materials, high conductivity, and good reversibility. This paper systematically reviews the research status and development prospects of PANI-based flexible energy storage devices. First, the basic properties and core energy storage mechanisms of PANI are described. Then, the latest research progress of PANI-based flexible supercapacitors and flexible rechargeable batteries is summarized. Meanwhile, the key bottlenecks in this field are pointed out, including low energy density, poor cycling stability, and immature device fabrication technology. Three targeted optimization strategies are concluded: molecular engineering and doping system optimization, nanostructure regulation and composite design, interface engineering and compatibility improvement. In addition, the emerging application of PANI in photo-enhanced flexible energy storage devices is introduced. As a p-type semiconductor, PANI can form heterojunctions with photoactive components to realize photo-assisted charging. Relevant studies have achieved breakthroughs in aqueous zinc-ion batteries, realizing performance improvement and multi-mode operation. Finally, the future development of PANI-based flexible energy storage devices is prospected, aiming to provide systematic theoretical reference and guidance for the rational design and industrial application of PANI-based energy storage materials.

Keywords: polyaniline; flexible energy storage device; electrochemical performance; photo-enhanced batteries

1. Introduction

With the rapid evolution of the global electronics industry toward flexibility, portability and wearability, the large-scale application of emerging products such as foldable-screen smartphones, electronic skin, and flexible medical monitoring devices have imposed unprecedented requirements on supporting energy storage devices. These devices demand not only fundamental electrochemical properties including high energy density, high power density, long cycle life, and high safety[1], but also exceptional mechanical flexibility, stretchability, and twistability[2]. Conventional rigid energy storage devices (e.g., commercial lithium-ion batteries) are constrained by their electrode architectures, packaging formats, and material systems, and cannot accommodate the complex deformation requirements of flexible electronics. Consequently, the development of novel flexible energy storage materials and devices has become a cutting-edge research area at the intersection of new energy and electronic information technologies.

Among various candidate materials for flexible electrodes, conjugated conducting polymers have emerged as one of the most important research systems for flexible energy-storage devices owing to their intrinsic electronic conductivity, reversible redox activity, and excellent molecular designability. Polyaniline (PANI) is the most extensively studied and industrially promising representative among conjugated conducting polymers, ranking alongside PPy and PEDOT as one of the three mainstream conducting polymers. Compared with PPy and PEDOT, polyaniline has become a key functional material in fields such as electrochemical energy storage, anti-corrosion coatings, sensing and electromagnetic shielding due to its high theoretical specific capacity, low synthesis cost, widely tunable electrical conductivity and various redox states[3]. It is also the most maturely applied conductive polymer matrix in aqueous energy storage devices including supercapacitors and aqueous zinc-ion batteries.

Since the electrochemical energy-storage properties of conducting polymers were discovered in the 1980s, research on PANI-based energy-storage materials has evolved over more than 40 years, progressing from fundamental material synthesis and mechanism investigation to device structural design and scenario-based applications. In recent years, with the explosive growth of the flexible electronics industry, PANI-based flexible energy-storage devices have achieved a series of breakthroughs. However, several critical issues remain to be addressed: insufficient cycling stability, significant volume effects during charge–discharge, immature large-area device fabrication, poor interfacial compatibility, and severe performance degradation in practical applications. These bottlenecks still hinder the transition of PANI-based systems from laboratory research to industrial mass production.

Based on the above advantages and shortcomings, this paper systematically combs the research status and development context of PANI-based flexible energy storage devices. First, we elaborate on the molecular structure, intrinsic semiconductor properties and core electrochemical energy storage mechanisms of PANI; then comprehensively summarize the latest research progress of PANI in flexible energy storage devices; deeply analyze the core bottlenecks existing in current research and applications; specifically summarize the mainstream performance optimization strategies and technical paths; at the same time, introduce the expanded application of PANI in the emerging field of photo-enhanced flexible energy storage devices; finally, look forward to the future development direction of this field, aiming to provide a reference for the high-performance, multifunctional and industrialized development of PANI-based flexible energy storage devices.

2. Fundamental properties and energy storage mechanism of polyaniline

2.1. Molecular structure and intrinsic semiconductor properties of PANI

PANI is a conjugated conducting polymer formed by oxidative polymerization of aniline monomers. Its molecular backbone consists of benzene and quinone rings alternately linked by imino groups, exhibiting multilevel tunable redox states and a unique proton doping mechanism, which are the fundamental origins of its combined electrical conductivity and electrochemical activity. The benzene–quinone coexistence model proposed by MacDiarmid in 1987 is currently the widely accepted structural model for polyaniline[4]. The molecular chain of polyaniline consists of alternating reduced units (phenylenediamine units) and oxidized units (quinonediimine units). It exhibits several distinct states: leucoemeraldine base (LEB, fully reduced base), emeraldine base (EB, intermediate oxidation state base), pernigraniline (PNB, fully oxidized state), leucoemeraldine salt (LES, fully reduced salt), and emeraldine salt (ES, intermediate oxidation state salt, with the highest electrical conductivity, reaching up to 100 S cm^{-1}). The chemical structure of polyaniline and the interconversion between these states are illustrated in Figure 1(a).

The doping mechanism of PANI differs from traditional inorganic semiconductors: no electron transfer occurs during doping, and charge carriers are generated solely via protonation by protonic acids. Protons bind to imine nitrogen atoms in the molecular chain, delocalizing positive charges along the conjugated backbone and forming a highly conductive polaron lattice. This doping process is highly reversible; dedoping can be achieved through acid–base neutralization, allowing reversible tuning of PANI's conductivity and electrochemical activity[5,6]. Meanwhile, the type and structure of dopants critically determine PANI performance: PANI doped with small inorganic acids (HCl, H_2SO_4, etc.) exhibits high conductivity but poor stability, undergoing easy dedoping in neutral or alkaline environments. In contrast, PANI doped with large organic acids (camphorsulfonic acid, dodecylbenzenesulfonic acid, etc.) or polymeric acids (polystyrenesulfonic acid, etc.) forms stable supramolecular structures with the dopant, significantly enhancing doping stability, environmental tolerance, and film flexibility[7–9].

As a typical p-type conjugated semiconductor in its intrinsic state, PANI has a bandgap of approximately 2.8 eV. Proton doping effectively modulates its band structure and carrier concentration, shifting the Fermi level toward the valence band and greatly enhancing hole mobility and electrical conductivity[5,10,11]. Meanwhile, the conjugated backbone of PANI enables broad visible-light absorption and favorable photoelectric conversion properties, laying the foundation for its application in photo-enhanced energy-storage devices. Furthermore, the rigid conjugated structure combined with the designable flexible segments of PANI chains provides balanced mechanical strength and film-forming ability. Molecular modification can further improve its flexibility and processability to meet the deformation requirements of flexible energy-storage devices[12,13].

2.2. Core charge storage mechanism of PANI in electrochemical energy storage

The charge storage behavior of PANI in electrochemical energy-storage devices is mainly governed by its highly reversible proton doping/dedoping and redox reactions. Depending on the device type and electrolyte system, its energy-storage mechanism can be classified into two categories: pseudocapacitive energy storage and battery-type redox energy storage. The core difference between them lies in the kinetic characteristics of electrochemical reactions and the mode of charge storage.

2.2.1. Pseudocapacitive charge storage mechanism

Pseudocapacitive energy storage is the dominant charge-storage mechanism of PANI in supercapacitors. It belongs to Faradaic reactions, featuring fast charge-transfer kinetics and highly reversible charge–discharge behavior, enabling both high power density and high specific capacity[14,15]. The pseudocapacitive storage of PANI mainly involves two key processes:

(a) Reversible proton doping/dedoping: In acidic electrolytes, PANI undergoes successive protonation and deprotonation during charge–discharge. Protons migrate rapidly between the electrolyte and the PANI backbone, accompanied by anion insertion and extraction, enabling fast charge storage and release. During this process, PANI undergoes two consecutive reversible redox reactions among leucoemeraldine, emeraldine, and pernigraniline states, corresponding to two characteristic redox peaks, as shown in **Figure1(b)**[16]. The transition between LEB and EB shows the highest reversibility and contributes the majority of the pseudocapacitive capacity[17,18].

(b) Synergistic contribution of electric double-layer capacitance: In nanostructured or composite PANI systems, the high specific surface area of the electrode enables the formation of an electric double layer at the electrode/electrolyte interface, where ions are stored via electrostatic adsorption, providing additional double-layer capacitance. Although this contribution is lower than that of pseudocapacitance, its faster kinetic behavior significantly improves the rate capability and power density of the electrode[19,20].

Moreover, the pseudocapacitive energy storage behavior of PANI is highly dependent on electrolyte pH. In acidic electrolytes (pH<2), proton doping/dedoping of PANI is highly reversible, yielding optimal conductivity and electrochemical activity. In neutral electrolytes, reduced proton concentration readily causes dedoping, resulting in a significant decrease in conductivity and redox activity[21]. In alkaline electrolytes, the quinoid structure of PANI undergoes irreversible degradation, leading to permanent deactivation of active sites. This characteristic is one of the key factors limiting the application of PANI in alkaline electrolyte systems[22].

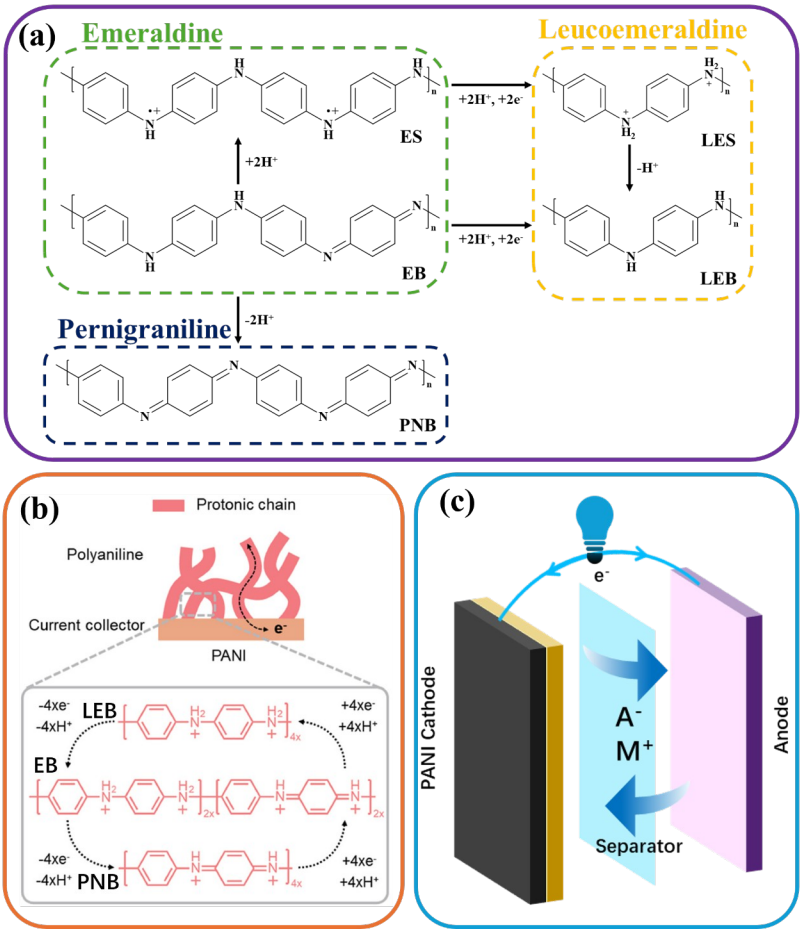

Figure 1. Structure and energy storage mechanism of polyaniline: (a) Schematic diagram of the conversion of polyaniline between different oxidation states, (b) Schematic diagram of electron transport pathways and the possible redox reactions of polyaniline under strong acidic condition[16], (c) Schematic diagram of the classic Rocking-Chair energy storage mechanism of polyaniline batteries, where A^- refers to the anion, and M^+ refers to the metal cation.

2.2.2. Battery-type redox energy storage mechanism

In rechargeable secondary battery systems, the charge storage mechanism of PANI is mainly the rocking-chair type as shown in **Figure 1(c)**, and its core energy storage mechanism is anion doping/dedoping reaction. During the charging process, PANI molecular chains are oxidized, and imino groups (-N=) lose electrons and convert into cationic radicals (polarons). Anions in the electrolyte (such as PF_6^-, ClO_4^-, $TFSI^-$) intercalate between PANI molecular chains to compensate for positive charges. During the discharging process, PANI molecular chains are reduced, electrons return to the main chains, and anions are deintercalated from between the molecular chains back into the electrolyte. The overall reaction of this process can be expressed as:

$$PANI + x\,A^- \leftrightarrows PANI^{x+}\left(A^-\right)_x + x\,e^- \quad (1)$$

Among them, A^- stands for the anion in the electrolyte, and x represents the doping degree.

In aqueous electrolytes and high-concentration electrolytes, apart from anion doping, cations (H^+, Li^+, Na^+, K^+) also participate in electrochemical reactions to form an "anion-cation co-doping" mechanism, which represents an important breakthrough in the research on the energy storage mechanism of PANI in recent years. What's more, PANI can also serve as functional components such as conductive substrates, hosts for active sites, and interfacial catalytic layers to participate in electrochemical reactions.

In lithium-ion batteries, PANI mainly relies on p-type doping/dedoping as the core mechanism, realizing the synergistic intercalation/deintercalation of Li^+ and electrolyte anions through reversible redox transitions between benzene and quinone rings on the conjugated backbone[23]. Meanwhile, its high conductivity constructs a continuous electron transport network, reducing electrode polarization and charge-transfer impedance. The flexible segments effectively buffer volume changes of active materials during cycling, stabilizing the electrode structure and suppressing interfacial side reactions. PANI is widely used as a cathode active material, conductive coating layer, or structural reinforcing component[24–26].

In sodium-ion batteries, PANI follows a similar mechanism. However, due to the larger ionic radius and slower diffusion kinetics of Na^+[27], its role shifts more toward providing a flexible framework and regulating ion pathways. The relaxed polymer chains reduce Na^+ transport resistance and enhance rate capability[28]. Meanwhile, PANI can serve as a composite modification layer for carbon- or alloy-based anodes to alleviate volume expansion and stabilize the solid–liquid interface. Although its reaction potential is like that in lithium-ion batteries, the ion coordination and transport behavior differ significantly[29].

In aqueous zinc-ion batteries, the mechanism of PANI is dominated by proton-coupled and electron transfer, accompanied by co-insertion of H^+/Zn^{2+} and N–Zn coordination. The doping/dedoping process is faster and exhibits more pronounced pseudocapacitive characteristics[30]. So, PANI not only contributes high specific capacity but also can optimize the electrode–electrolyte interface, suppressing Zn dendrite growth and water-splitting side reactions. Its energy-storage kinetics and potential window are distinctly different from those in organic electrolytes, relying more on a rapid dual H^+/Zn^{2+} transport mechanism[31,32].

In summary, the charge-storage capability of PANI fundamentally originates from reversible redox reactions and ion doping/dedoping in its conjugated backbone, which are highly correlated with molecular structure, morphology, composite design, and electrolyte conditions. Through molecular engineering, structural regulation, and composite modification, the energy-storage behavior of PANI can be precisely tuned to meet the performance requirements of various flexible energy-storage devices.

3. Research progress of PANI in flexible energy storage devices

With the rapid development of flexible electronics, PANI-based flexible energy-storage devices have become a research hotspot. Through electrode structure design, device configuration optimization, and system matching, researchers have developed a series of PANI-based devices with excellent electrochemical performance and mechanical flexibility. Among these, flexible supercapacitors and flexible rechargeable batteries are the most mature systems with the broadest application prospects.

3.1. PANI-based flexible supercapacitors

However, pure PANI suffers from poor mechanical flexibility, severe volume expansion, and insufficient cycling stability, making it unsuitable for direct use as a flexible electrode. Therefore, current research mainly focuses on composite modification and structural design to fabricate PANI-based composite electrodes with both high electrochemical performance and excellent flexibility. The mainstream strategies include PANI/carbon and PANI/metal oxide composite flexible electrodes.

PANI/carbon composite flexible electrodes represent one of the most extensively studied and technically mature approaches, whose core lies in using carbon materials' superior flexibility, high specific surface area, excellent conductivity, and chemical stability to compensate for the shortcomings of pure PANI[33]. The

introduction of carbon not only effectively alleviates volume expansion of PANI during cycling and reduces active material detachment, but also constructs a continuous conductive network to accelerate electron and ion transport, while enhancing mechanical strength and flexibility to withstand bending, folding, and other deformations[34].

In recent work, PANI was synthesized on carbon nanotubes via liquid crystalline wet-spinning method, yielding a composite electrode with a specific capacitance of 1714 F g^{-1}, nearly 100% capacitance retention after 100,000 cycles, and stability over 10,000 mechanical deformations[35]. Graphene's ultrahigh surface area and mechanical strength enable significant capacitance enhancement. Using chemically converted graphene (CCG) and PANI nanofibers (PANI-NFs), layer-structured composite films (G-PANI) were fabricated by vacuum filtration, with conductivity up to 5.5×10^2 S m^{-1}. The corresponding supercapacitor delivered 210 F g^{-1} at 0.3 A g^{-1}, with greatly improved stability and rate capability, as well as outstanding mechanical flexibility[36]. Flexible carbon substrates such as carbon cloth and carbon fibers can directly serve as skeletons for in situ growth of PANI, simplifying fabrication while preserving flexibility and structural integrity[19].

Current research focuses on optimizing composite ratios, interfacial bonding, and novel structures via in situ polymerization or hydrothermal methods to minimize interfacial resistance. For instance, nanostructured porous carbon–PANI coated carbon cloth (PANI-CC, shown in **Figure 2(a)**) prepared by in situ chemical oxidation on highly flexible conductive carbon cloth (CC) achieved 691 F g^{-1} at 1 A g^{-1}, 94% retention after 2000 cycles, and 72% capacitance retention at a bending angle of 140°, as shown in **Figure 2(b, c)**[37].

PANI/metal oxide composite flexible electrodes are mainly designed to address the limited specific capacity and insufficient redox activity of pure PANI. By introducing metal oxides with high theoretical capacity, synergistic effects are achieved to enhance overall electrochemical performance[38]. Metal oxides (e.g., MnO_2) provide abundant redox sites and high capacity; when combined with PANI, they benefit from improved electron transport, while PANI compensates for their poor conductivity.

For example, a one-step method was used to synthesize PANI/MnO_2 on carbon cloth (CC), forming a supercapacitor electrode (**Figure 2(d)**) that delivered 1.7 F cm^{-1} at 1 mA cm^{-1}, better than pure PANI/CC and MnO_2/CC, with excellent bending and cycling stability (**Figure 2(e, f**)) [39]. In another study, $Ni_3V_2O_8$@PANI prepared via in situ chemical bath exhibited an ultrahigh specific capacitance of 2565.7 F g^{-1} within a wide potential window of 0–1.6 V and good rate capability[40]. Furthermore, Ni–Co nanoparticles supported on polyaniline-salphen (PS) were in situ polymerized on CC (Ni-Co@PS-CC), achieving 1447.2 F g^{-1} at 0.5 A g^{-1} and 95.9% retention after 5,000 cycles at 9.0 A g^{-1}. When applied in asymmetric wearable supercapacitors, it provided 70.01 F g^{-1} and an energy density of 23.46 Wh kg^{-1} at 800 W kg^{-1} (**Figure 2(g-i)**)[41].

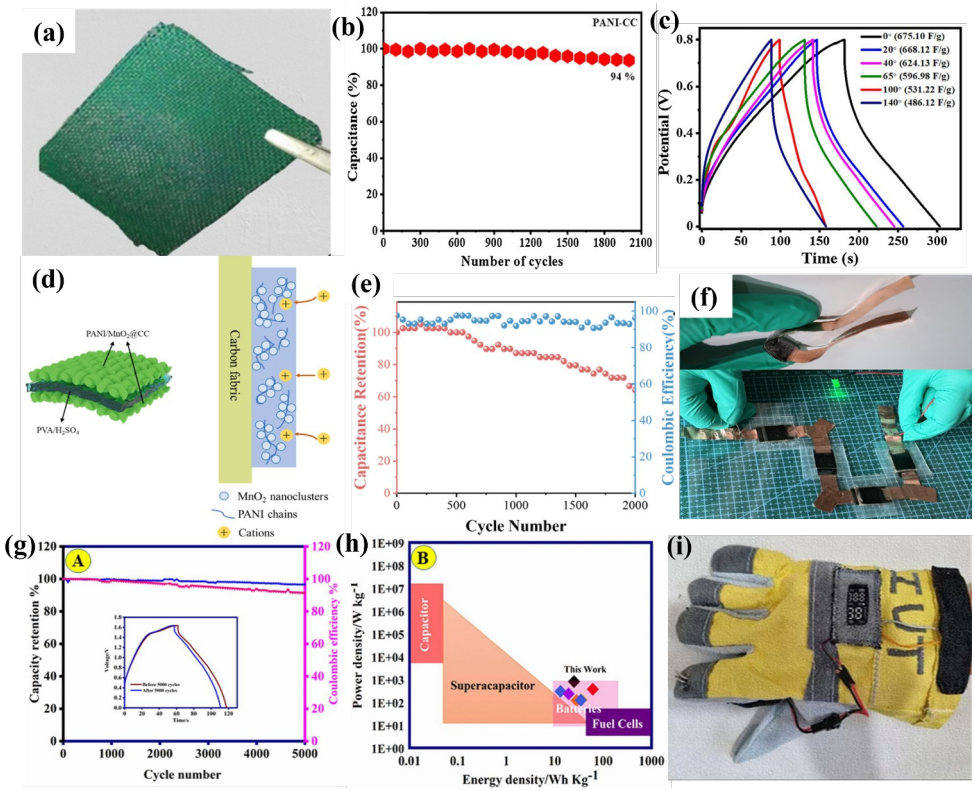

Figure. 2. Different PANI-based flexible supercapacitors: (a) Digital images showing substrate after polymerization (PANI–CC), (b) Stability test up to 2000 GCD cycles for PANI-CC and (c) GCD (at 1 A/g) of PANI-CC flexible SC at each bending angle[37]; (d) Charge storage mechanism, (e) Cycling stability at 2.5 mA cm^{-2} of MnO_2/PANI@CC and (f) Optical image of the supercapacitor under bending (top) and the symmetric supercapacitors with 4 in series lighting an LED (3 V) (bottom)[39]; (g) Ni-Co@PS-CC//AC devise stability test at 9.0 A g−1 (the inset indicates the GCD of the primary electrode and after 5000 cycles), (h) Ragone plot of Ni-Co@PS-CC//AC device, (i) the digital image of a wearable supercapacitor that has been integrated into a glove for the purpose of powering an oximeter[41].

Besides the two mainstream categories above, recent studies have explored composite systems of PANI with other polymers, metal-organic frameworks (MOFs), MXene, metal hydroxide and other emerging materials to further extend the performance limits of PANI-based flexible electrodes. For instance, blending PANI with flexible polymers (e.g., PVA, PAAm, cellulose) improves flexibility and mechanical durability[13]; hybridization with MOFs utilizes their high surface area and tunable pores to optimize ion pathways and enhance storage performance[42]; combining with MXene leverages its excellent conductivity and layered structure to build efficient conductive networks, alleviating PANI swelling and structural collapse and boosting electrochemical kinetics[43,44]; composited with $Ce(OH)_3$ via the microwave-assisted synthesis, the constructed $Ce(OH)_3$/PANI nanocomposite material features a porous microstructure, which greatly facilitates the diffusion of electrolyte ions and charge storage[1].

Overall, research on PANI-based composite flexible electrodes centers on enhancing flexibility and improving electrochemical performance, using synergistic composites and structural engineering to overcome intrinsic drawbacks of pure PANI. Current challenges remain weak interfacial bonding, difficult structure control, and complex scalable fabrication[45]. Future directions will focus on developing novel composite systems, clarifying interfacial mechanisms, optimizing green and scalable preparation, and validating performance in practical flexible supercapacitors, driving PANI-based electrodes toward high-performance,

low-cost, and industrial-scale applications.

3.2. PANI-based flexible rechargeable batteries

Compared with flexible supercapacitors, flexible rechargeable batteries have become a key research direction for meeting the long-endurance demand of flexible electronic devices due to their higher energy density. As a typical conductive polymer, polyaniline (PANI) features high conductivity, excellent structural designability, and multifunctionality. It has been widely applied in various flexible rechargeable battery systems, including flexible lithium-ion, sodium-ion, and zinc-ion batteries. Its core roles involve serving as active electrode material, constructing conductive networks, structural reinforcement, and interfacial modification, which effectively improve capacity, cycling stability, and mechanical flexibility of the batteries.

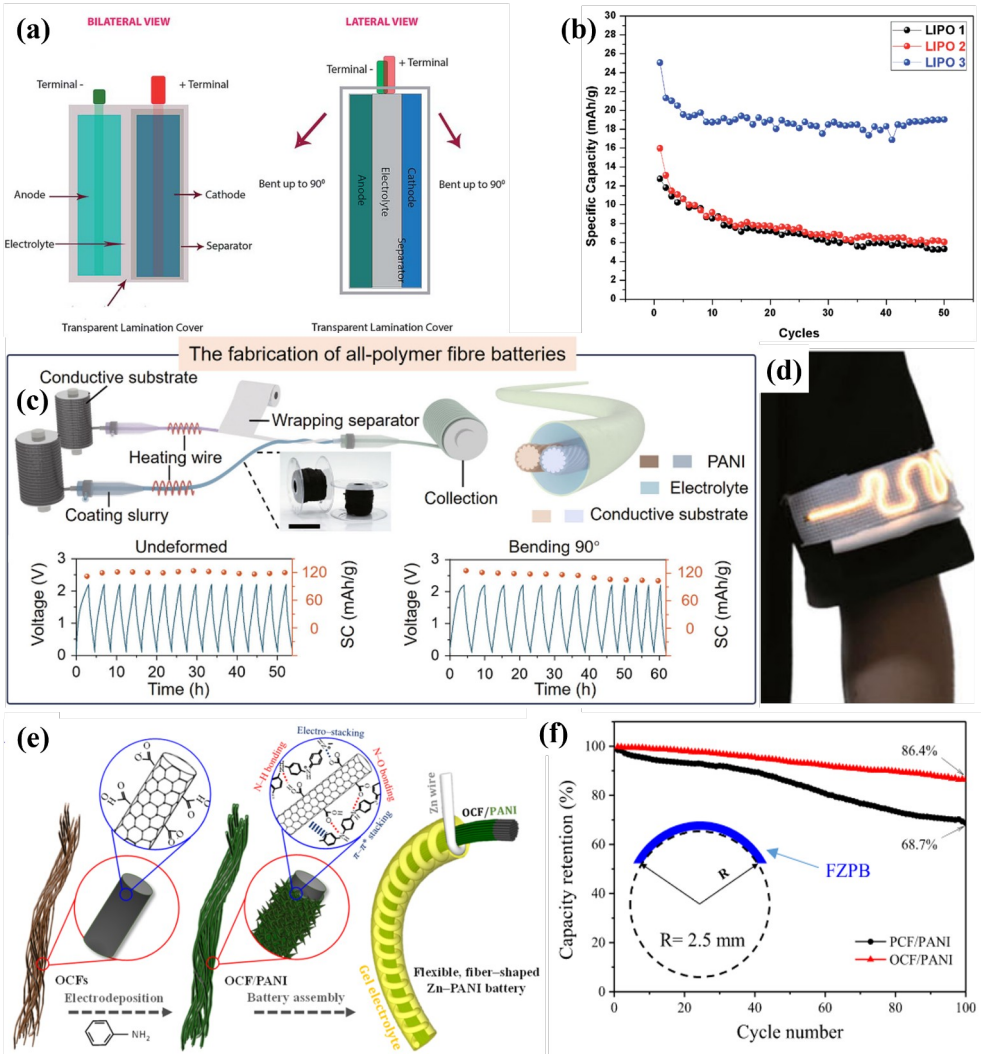

Figure. 3. Different PANI-based flexible rechargeable batteries: (a) Schematic representation and (b) Specific capacity versus charge–discharge cycle number for LIPO-PANI pouch cell[46]; (c) Schematic of continuous fabrication of all-polymer FSIBs and its GCD profiles under different deformations and (d) Photograph of a flexible LED powered by flexible films all-polymer FSIBs group[47]; (e) Schematic preparation of OCF/PANI electrode-based flexible FZPBs and (f) Long bending test[48].

3.2.1. PANI in flexible Li-ion batteries

Flexible lithium-ion batteries (FLIBs) are the most widely used energy-storage devices in flexible electronics. Their key requirements are high energy density, good mechanical flexibility, and cycling stability. With its multifunctional properties, PANI can act as an anode material, cathode coating, or electrolyte additive, enabling multi-dimensional performance optimization.

For cathode modification, PANI is used to coat or composite with layered oxides ($LiCoO_2$, $LiNi_xCo_yMn_zO_2$) and $LiFePO_4$ (LFP). It forms a continuous conductive network, reduces interfacial resistance, accelerates electron and Li^+ transport, suppresses particle detachment and electrolyte corrosion, and greatly extends cycling life[49].

For example, researchers first prepared Li-doped polyaniline (LiPO) and combined it with $LiFePO_4$ and $LiMn_2O_4$ to form flexible cathodes. Using a gel polymer electrolyte (PEO), flexible pouch LIBs were assembled in **Figure 3(a)**, overcoming the rigidity issue of conventional electrodes for flexible wearable devices while achieving environmental friendliness and stable cycling. The battery delivered a maximum discharge capacity of 21 mAh g^{-1} in **Figure 3(b)**, Coulombic efficiency stably at 99.99%, and maintained an open-circuit voltage of 0.6 V even under 90° bending, providing a new route for flexible LIBs[46].

As an anode material, the flexible structure of PANI effectively relieves volume expansion during Li^+ intercalation/deintercalation and prevents electrode cracking. Meanwhile, its high conductivity accelerates Li^+ transport kinetics, addressing the low conductivity and large volume expansion of conventional carbon-based anodes[26]. Studies show that PANI composites with graphite and silicon-based materials not only improve flexibility and mechanical strength but also significantly enhance specific capacity and cycling life, meeting the long-term demands of flexible batteries. For example, PANI was covalently bonded to nano-Si/expanded graphite (Si@EG), suppressing Si nanoparticle agglomeration, forming a robust conductive network, and effectively mitigating volume expansion of silicon anodes[50].

In addition, PANI can serve as an electrolyte additive. Its functional groups interact with Li^+ to enhance ionic conductivity and optimize transport pathways, further boosting overall performance of flexible LIBs[51].At present, PANI-based flexible LIBs have achieved high energy density and stable electrochemistry under repeated bending/folding, basically meeting the energy-storage requirements of flexible wearable devices such as smart bracelets.

3.2.2. PANI in flexible Na-ion batteries

Flexible sodium-ion batteries (FSIBs) are promising for large-scale flexible electronics due to abundant Na resources and low cost. PANI acts as active material, conductive agent, and structural stabilizer, addressing key issues such as large Na^+ radius, slow diffusion, and poor structural stability[27].

As a cathode active material, PANI enables reversible Na^+ insertion/extraction via redox reactions, offering high theoretical capacity and good rate capability. Nanowires, thin films, and porous structures can be tailored by polymerization to enlarge contact area and accelerate kinetics. Pure PANI flexible cathodes show stable Na-storage performance in both aqueous and organic electrolytes.

For example, an all-polymer symmetric aqueous SIB was designed with PANI as both cathode and anode, using NaTFSI-PEGDME aqueous polymer electrolyte in **Figure 3(c, d)**. The cell delivered 139 mAh g^{-1} in capacity and 153 Wh kg^{-1} in energy density, with 92% capacity retention after 4800 cycles, creating a new pathway for sustainable wearable energy storage device[47].

3.2.3. PANI in flexible Zn-ion batteries

Aqueous zinc-ion batteries (AZIBs) are ideal for flexible wearable electronics due to their high safety, low

cost, environmental friendliness, and high theoretical capacity. Among them, PANI is one of the most widely studied cathode materials[52].

Research on PANI-based flexible AZIBs mainly focuses on cathode modification and device structural design. In cathode engineering, molecular engineering, nanostructure control, and composite strategies are used to overcome the drawbacks of pure PANI in neutral/weakly acidic electrolytes, such as dedoping, rapid capacity fading, and poor rate performance.

To strengthen the interfacial adhesion between PANI and the current collector, our group previously developed a novel flexible fiber-shaped zinc–polyaniline battery (FZPB). Carbon fibers were pretreated by O_2^+ plasma bombardment via electron cyclotron resonance (ECR), which enlarged specific surface area and total pore volume while introducing abundant oxygen-containing groups. PANI was then in-situ electropolymerized on the O_2^+ modified carbon fibers (OCF), forming a uniform, high-loading OCF/PANI electrode, as shown in **Figure 3(e)**. The assembled FZPB exhibited 95.39% capacity retention after 200 cycles at 0.1 A g^{-1}, 83.96 mAh g^{-1} at a high rate of 2 A g^{-1} and outstanding flexibility: 86.4% capacity retention after 100 bends at a 2.5 mm bending radius in **Figure 3(f)**, making it highly promising for wearable energy devices[48].

For device configuration, researchers have developed a methylsulfonic acid-doped PVA gel electrolyte for fiber-shaped quasi-solid-state Zn–PANI batteries. The relatively large methanesulfonate molecules in the solid electrolyte block water from contacting the active materials (PANI and Zn), while small chloride anions enable efficient doping of PANI. The synergistic effect of dual-anion doping and water trapping suppresses PANI degradation and Zn corrosion, leading to exceptional performance: 88.1% capacity retention after 2,000 cycles and 92.7% retention after 500 bending cycles at a 2.5 mm bending radius.Furthermore, all-carbon-yarn flexible Zn–PANI batteries (Fs-ZPB) using this electrolyte fully meet the requirements for practical wearable applications[53].

3.2.4. Other PANI-based flexible batteries

Apart from the above three types of PANI-based flexible batteries, many emerging battery have also attempted to introduce flexibility by leveraging the excellent properties of PANI.

For instance, researchers have for the first time constructed full metal-free flexible ammonium-ion batteries, adopting polyaniline as the anode and polypyrrole as the cathode, matched with quasi-solid-state (QSS) hydrogel electrolyte that is prepared with edible xanthan gum and $(NH_4)_2SO_4$ solution. This quasi-solid-state battery can still maintain a high capacity retention rate under mechanical deformations such as bending and twisting, possessing both mechanical flexibility and electrochemical performance[54].

In addition, some researchers have also proposed a polyaniline/single-walled carbon nanotubes (PANI/SWCNTs) composite films and protonated the PANI nanorods. The protonation endows PANI with more active sites and enhanced conductivity. Hyper self-protonated PANI (PANI(H^+)) exhibits reversible $AlCl_2^+$ intercalation/de-intercalation during the discharge/charge process. As a result, the discharge capacity of the Al/PANI(H^+) battery is twice as high as that of the initial composite films. PANI(H^+)@SWCNT electrodes also have a stable cycling life with only 0.003 % capacity decay per cycle over 8000 cycles. Owing to the excellent mechanical properties, PANI(H^+)@SWCNT composite films can act as the electrodes of flexible aluminum-ion batteries[55].

Other researchers have introduced PANI/carbon cloth into magnesium-ion batteries (MIBs). This cathode not only solves the problem of slow diffusion rate in MIBs, but also makes the flexible fabrication of MIBs possible[56].

In summary, this chapter systematically summarizes the research progress of PANI-based flexible energy

storage devices in supercapacitors and rechargeable batteries. It clarifies that composite modification and structural design are the core approaches to solving the inherent defects of pure PANI such as poor mechanical properties, volume expansion and unstable cycling performance. It also sorts out the performance advantages and application achievements of different composite systems, among which aqueous zinc-ion batteries have achieved breakthrough progress in highly flexible devices. Nevertheless, the above achievements are still confined to the laboratory verification stage, and the core bottlenecks at the material intrinsic and device levels have not been fundamentally resolved, which further leads to in-depth analysis of existing problems and discussion on targeted optimization strategies in the follow-up content.

4. Bottlenecks and shortcomings of PANI-based flexible energy storage devices

Despite the breakthroughs of PANI-based flexible energy-storage devices in flexible supercapacitors and batteries, critical bottlenecks remain in intrinsic material properties, fabrication processes, interface engineering, and practical environmental adaptation. These challenges severely limit further performance improvement and commercialization, representing urgent pain points in flexible PANI-based energy storage device.

4.1. Intrinsic defects of PANI material

Intrinsic defects of PANI are among the fundamental constraints limiting the performance and application of its flexible energy-storage devices. The most critical issues are poor cycling stability and severe volume expansion during charge/discharge process, which interact synergistically and accelerate performance degradation[57–59].

For cycling stability, as a conjugated polymer, PANI undergoes reversible structural changes during electrochemical redox: repeated proton doping/dedoping causes chain distortion and cleavage, gradually destroying conjugation and losing active sites, leading to continuous capacitance decay and short cycle life[60]. Pure PANI electrodes typically retain less than 50% capacity after hundreds to thousands of cycles[25,32,61], failing long-term flexible device requirements. Moreover, low crystallinity and weak interchain interactions cause chain agglomeration and detachment under cycling stress, further worsening stability[34,62].

The volume expansion issue is directly related to PANI's doping/dedoping process. During proton doping, protons and anions insert into the interchain space, increasing chain distance and causing macroscopic volume expansion. Upon dedoping, the inserted ions depart, chains contract, and volume recovers[57].

Repeated "expansion and recovery" cycles generate persistent mechanical stress, causing cracking and pulverization of PANI, breaking interfacial bonding with current collectors and electrolytes, increasing contact resistance, and hindering charge transfer. This leads to simultaneous degradation in electrochemical performance and mechanical flexibility. Volume expansion also impairs dimensional stability, making it incompatible with the strict volume requirements of miniaturized, thin flexible electronics, limiting its application in compact devices[59,63].

4.2. Problems in device fabrication and interface engineering

Besides intrinsic material defects, poor fabrication processes and weak interface engineering severely hinder industrialization of PANI-based flexible devices. In flexible energy storage, current collectors must collect current, provide mechanical support, and withstand repeated bending and twisting. Common flexible current collectors include metal foils (Cu, Al), conductive fabrics, and carbon-based materials (graphene, CNT films).

However, as a polymer, PANI has low surface energy and weak polarity, resulting in weak physical adsorption and chemical bonding with both metal and carbon/textile substrates, leading to frequent delamination[64–67].

Weak interfacial adhesion causes a series of issues. On one hand, during charge-discharge cycling, the contact resistance between the electrode and current collector increases significantly, reducing charge-transfer efficiency and decreasing the device power density, and even leading to localized heating and aggravated energy loss[68]. On the other hand, under repeated bending and twisting in flexible applications, stress concentration at the interface induces delamination and detachment of the PANI active layer from the current collector. This not only causes the loss of active material but also results in internal short circuits and abrupt performance degradation, severely impairing the lifespan and safety of the device[69]. Furthermore, conventional preparation methods such as coating and drop-casting are commonly used to load PANI onto current collectors, which fail to achieve uniform integration between the active material and the substrate, thereby further exacerbating weak interfacial adhesion[70]. Meanwhile, poor electrolyte wettability and accumulation of interfacial reaction products act synergistically with weak adhesion, further limiting the improvement of overall device performance[71].

5. Performance optimization strategies of PANI-based flexible energy storage devices

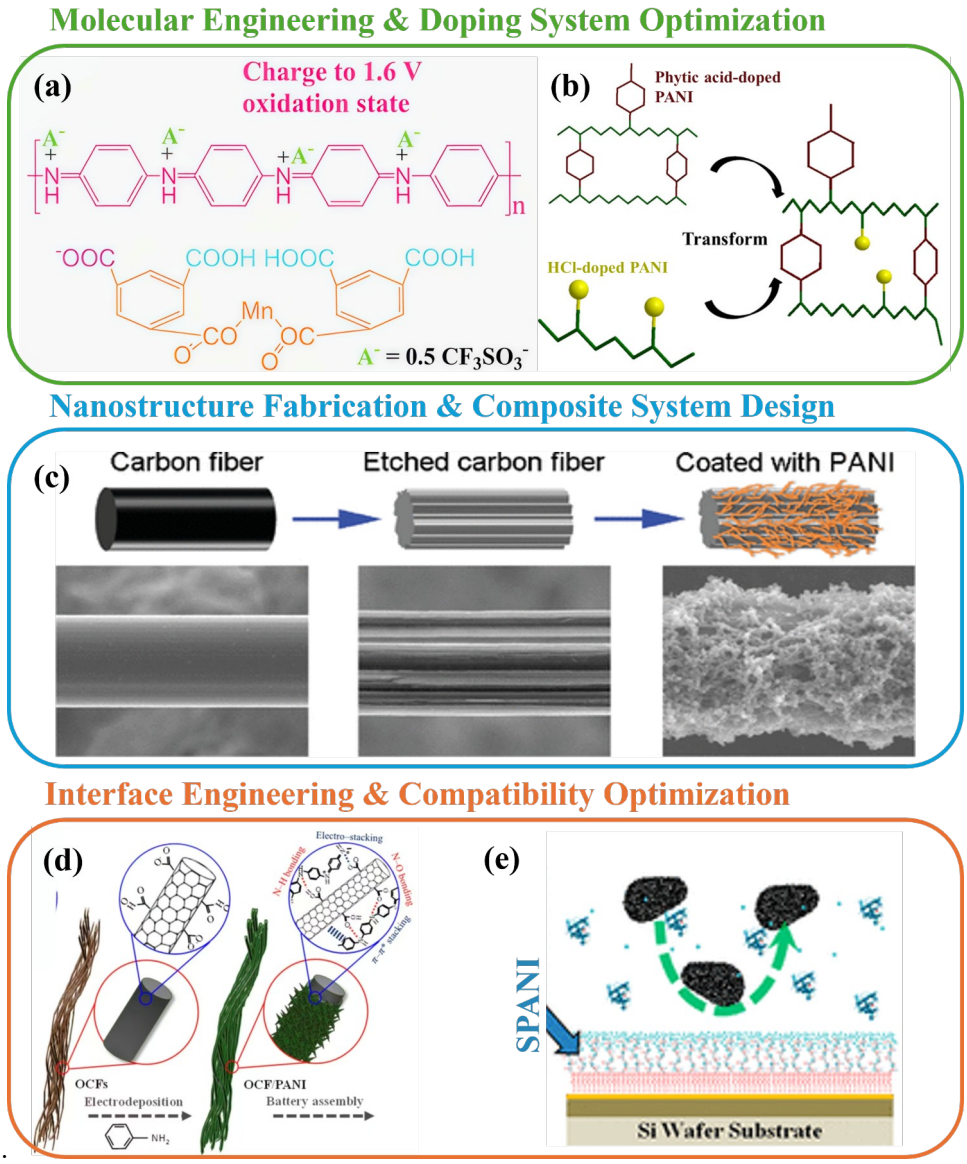

Figure 4. Different optimization strategies of PANI-based flexible energy storage device: (a) The energy storage mechanism of the proton self-doped PANI[72], (b) PANI architecture by binary (weak and strong) acid doping[73], (c) SEM images and schematic diagrams of electro-etched carbon fiber and CF/PANI electrodes synthesized therefrom[74], (d) Schematic diagram of electrode-current collector interface optimization by using oxygen-containing functional groups[48] and (e) Schematic diagram of electrode-electrolyte interface optimization by using self-doped sulfonated polyaniline[75].

Owing to its high conductivity, reversible redox activity, low cost, and facile synthesis, PANI has emerged as one of the most promising electrode materials for flexible energy-storage devices. Nevertheless, the practical application of polyaniline-based flexible energy-storage devices is still hindered by inherent drawbacks mentioned above. To address these issues, this work systematically reviews optimization strategies adopted in conventional energy-storage devices from three aspects: molecular structure regulation, nanostructure design, and interface engineering. It aims to provide theoretical guidance and technical support for the development of

high-performance polyaniline-based flexible energy-storage devices.

5.1. Molecular engineering and doping system optimization

Molecular engineering and doping system optimization serve as fundamental strategies for enhancing the conductivity, redox activity, and mechanical properties of polyaniline, which directly govern the energy storage performance and cycling life of flexible devices. Through approaches such as modifying the molecular structure, optimizing the doping system, and performing cross-linking modification, the inherent drawbacks of polyaniline can be effectively mitigated, leading to a remarkable enhancement in its comprehensive performance.

The conductivity and redox performance of polyaniline are closely related to its degree of protonation[76]. Covalent grafting of proton-donor functional groups (such as $-CF_3SO_3^-$, -COOH, -OH, etc.) onto polyaniline chains can effectively improve its protonation efficiency and proton transport rate in **Figure 4(a)**. These groups provide a stable proton source, thereby enhancing electrical conductivity[72,77]. Meanwhile, the grafted functional groups introduce steric hindrance, reducing chain aggregation, improving solubility and processability, and further enhancing the mechanical flexibility of the electrode[78,79]. For example, in the presence of the initiator aniline dimer, o-aminobenzenesulfonic acid undergoes rapid copolymerization with aniline to prepare SPANI nanoparticles, which can not only improve proton conductivity but also enhance the hydrophilicity of polyaniline, promote electrolyte infiltration, and accelerate the ion transport process at the electrode-electrolyte interface[80]. Furthermore, covalent grafting forms stable chemical bonds, preventing functional group detachment during charge–discharge cycling and thus improving the cycling stability of the device.

Doping is a key strategy for regulating the conductivity and redox activity of polyaniline. The choice of dopant type, doping concentration, and doping method directly determines the performance of PANI-based flexible energy storage devices[81]. Conventional dopants are mainly protonic acids (e.g., HCl, H_2SO_4), but they suffer from low doping stability and tend to leach during charge-discharge cycling, leading to performance degradation[82,83]. To address this issue, various modified doping strategies have been developed. On one hand, organic dopants with high molecular weight and strong stability (e.g., camphorsulfonic acid, dodecylbenzenesulfonic acid) are used to replace traditional inorganic acids. These dopants form strong interactions with polyaniline chains, enhancing doping stability and reducing leaching[84–86]. On the other hand, composite doping systems (binary or ternary) are constructed to achieve synergistic performance improvement. For example, combining strong inorganic acids with weak organic acids, as shown in **Figure 4(b)**, not only boosts conductivity but also improves mechanical flexibility and cycling stability[73,87]. In addition, doping methods can be optimized, including in-situ doping, post-doping, and electrochemical doping, to improve uniformity and efficiency, ensure full protonation of polyaniline chains, and maximize electrode performance[81,88].

Cross-link modification is an effective approach to enhance the mechanical stability and cycling performance of polyaniline. By introducing cross-linking agents, a 3D cross-linked network is formed among polyaniline chains, which effectively suppresses chain aggregation and strengthens both the mechanical strength and flexibility of polyaniline[59,89]. The cross-linked network not only improves mechanical properties but also mitigates volume expansion and contraction during charge-discharge cycling, thereby enhancing the cycling stability of the electrode[90,91].

In summary, the covalent grafting of proton-donor functional groups can simultaneously enhance the electrical conductivity, processability and cycling stability of materials. The adoption of organic macromolecular acids or inorganic-organic composite doping systems combined with optimized methods such as in-situ doping

can solve the problem of easy loss of traditional inorganic acid dopants. The 3D network constructed by cross-link modification can improve mechanical properties and alleviate volume expansion during charging and discharging. All the above strategies precisely regulate the molecular structure and electronic state of polyaniline, laying a core material foundation for subsequent structural fabrication and interface engineering.

5.2. Nanostructure fabrication and composite system design

The nanostructure and composite system design of polyaniline play a decisive role in the specific surface area, ion transport rate, and mechanical flexibility of electrodes. By tailoring the nanostructure of polyaniline and constructing composite systems with other functional materials, its inherent drawbacks (e.g., poor mechanical performance and low energy density) can be effectively compensated, thereby significantly improving the overall performance of flexible energy-storage devices.

Conventional polyaniline suffers from low specific surface area, slow ion transport, and poor mechanical flexibility, which restrict its application in flexible energy-storage devices. To overcome these limitations, researchers have fabricated polyaniline nanostructures such as nanofibers, nanotubes, and 3D porous architectures via morphology control, addressing the low crystallinity and high ion diffusion resistance of conventional PANI. Constructing nanostructured polyaniline greatly shortens the charge-transfer distance inside the material and relieves strain caused by electrochemical activity inhomogeneity within the electrode, thereby improving the mechanical stability of polyaniline[92,93]. For example, a rapid mixing method was employed to synthesize uniformly nucleated, fine, interconnected PANI nanofibers with high homogeneity and porosity. The symmetric supercapacitor based on these nanofibers delivered a capacitance of 378.8 F g^{-1} at 1 A g^{-1} with 90.33% capacitance retention after 3,000 cycles, providing a simple and scalable route for fabricating morphology-controllable polyaniline electrodes with enhanced performance[94].

Metal compounds exhibit high theoretical specific capacity and excellent redox activity, and their composites with polyaniline enable synergistic performance enhancement. On one hand, metal compounds compensate for the low specific capacity of polyaniline and boost the energy density of composite electrodes[25]. On the other hand, polyaniline acts as a conductive matrix to improve the conductivity of most poorly conductive metal compounds and suppress the aggregation of nanoparticles, thereby enhancing cycling stability and rate capability[95]. Typical metal compounds for hybridization with polyaniline include MnO_2, Co_3O_4, $Ni(OH)_2$, and MoS_2. For instance, PANI/MnO_2 composites integrate the high conductivity of PANI and the high specific capacity of MnO_2: PANI facilitates electron transfer in MnO_2, while MnO_2 provides additional redox sites, significantly improving the energy-storage performance of the electrode[39].

Carbon materials (e.g., graphene, carbon nanotubes, carbon fibers, porous carbon) possess high conductivity, large specific surface area, and excellent mechanical flexibility, making them ideal composites for enhancing the performance of polyaniline-based flexible energy-storage devices[96]. Compositing polyaniline with carbon materials not only strengthens electrical conductivity and mechanical flexibility but also increases the electrode specific surface area, providing more active sites for redox reactions and accelerating ion transport[97]. For example, electrochemical etching was used to activate carbon fibers and increase their specific surface area, followed by in-situ synthesis of PANI nanowires, as shown in **Figure 4(c)**. The resulting CF/PANI electrode achieved a high mass specific capacitance of 673 F g^{-1} and an area specific capacitance of 3.5 F cm^{-2}, offering a low-cost, scalable strategy for high-performance flexible energy-storage devices[74].

In summary, the construction of nanofibers, nanotubes and 3D porous structures can greatly shorten the charge transfer distance, alleviate internal electrode strain and improve mechanical stability. Composite modification with metal compounds can synergistically enhance specific capacity and redox activity, while

combination with carbon materials can build efficient conductive networks and boost electrode flexibility. Through multi-dimensional structural design and material synergy, these strategies achieve the simultaneous optimization of electrochemical and mechanical properties, representing the mainstream direction in the current development of polyaniline-based flexible electrodes.

5.3. Interface engineering and compatibility optimization

In polyaniline-based flexible energy-storage devices, interfaces between different components (e.g., electrode–current collector, electrode–electrolyte) directly govern electron transfer, ion transport, and mechanical stability. Poor interfacial compatibility leads to high interfacial resistance, slow ion diffusion, and even component delamination during bending or charge–discharge cycling, severely degrading device performance and lifespan. Therefore, interface engineering and compatibility optimization represent crucial strategies for enhancing the performance of polyaniline-based flexible energy-storage devices.

As a key component of flexible energy-storage devices, current collectors are responsible for electron collection and transport. The interface between polyaniline-based electrodes and current collectors must provide reliable electrical contact and mechanical adhesion to guarantee efficient electron transfer and stable mechanical performance under bending[98]. However, conventional current collectors (e.g., metal foils, carbon cloth) possess relatively smooth surfaces, resulting in weak interfacial adhesion between the PANI electrode and the substrate, which readily causes electrode delamination during bending or charge-discharge cycling. To address this issue, various interface optimization strategies have been developed. On one hand, surface modification of current collectors (e.g., roughening, conductive adhesive coating, functional group introduction) improves surface roughness and chemical reactivity, thereby strengthening mechanical adhesion and electrical contact at the interface[99]. For example, sandblasting or chemical etching of metal foils increases the contact area and enhances interfacial adhesion via mechanical interlocking[100]. In our previous work, carbon fibers were treated with O_2^+ plasma generated by electron cyclotron resonance (ECR), which introduced abundant oxygen-containing groups and significantly strengthened the bonding between PANI and carbon fibers in **Figure4(d)** [48].

The electrode-electrolyte interface serves as the site for redox reactions, and its compatibility directly determines ion transport rate, charge-transfer resistance, and cycling stability of the device. Poor compatibility induces passivation layer formation on the electrode surface, increasing interfacial resistance, slowing ion diffusion, and degrading cycling stability[101,102]. To optimize this interface, three strategies can be adopted: First, surface modification of the polyaniline electrode to improve hydrophilicity or lipophilicity and enhance electrolyte wettability. For example, grafting hydrophilic groups (e.g., -SO_3H, -COOH) onto PANI chains improves hydrophilicity and facilitates wetting by aqueous electrolytes, as shown in **Figure 4(e)** [20,75]. Second, optimization of the electrolyte system to match the polyaniline electrode[103]. Additives such as surfactants and ionic conductors can reduce interfacial tension, improve wettability and accelerate ion transport[104,105]. Moreover, gel or solid electrolytes form a stable interface, prevent liquid leakage, and enhance safety and cycling stability[106]. Third, construction of an interfacial modification layer between electrode and electrolyte, which not only improves compatibility but also suppresses side reactions and passivation layer formation, thereby boosting device performance[90].

In summary, roughening the current collector or introducing oxygen-containing functional groups can significantly enhance the interfacial adhesion between electrodes and current collectors, preventing the peeling of active layers during bending. Modifying electrode surfaces, optimizing electrolyte systems or introducing interfacial modification layers can improve electrolyte wettability, reduce interfacial impedance and inhibit side

reactions. These strategies unblock the transmission channels of electrons and ions from the perspective of device assembly, and serve as an important guarantee for the coordinated improvement of electrochemical performance and mechanical reliability of flexible devices.

6. Extended application of PANI in photo-enhanced flexible energy storage devices

6.1. Working mechanism of photo-enhanced energy storage devices and the adaptability of PANI

All the above-discussed electrochemical energy-storage devices only enable the conversion between electrical and chemical energy, yet cannot utilize solar energy. They rely on external photovoltaic modules to achieve a secondary conversion of light-electric-chemical energy, resulting in complex system architecture, high energy loss, and low overall efficiency[107]. To align with the sustainable development strategy of the energy sector and break the conventional paradigm of separated photovoltaic and energy-storage functions, researchers have innovatively proposed photo-enhanced rechargeable batteries, which integrate the photovoltaic effect and electrochemical energy storage into a single unit[108,109]. Compared with traditional flexible energy-storage devices, photo-enhanced flexible devices additionally incorporate photo-responsive components, enabling improved energy-storage performance under illumination. This manifests as enhanced charge-discharge capacity, higher charging efficiency, optimized cycling stability, and even self-charging via light without an external power supply, greatly expanding the application scenarios of flexible energy-storage devices[110].

The working mechanisms of photo-enhanced energy storage devices can be classified into two categories. One is the photo-assisted charging mechanism: under illumination, photoactive materials absorb light and generate charge carriers (electron–hole pairs). After separation, these carriers participate in the electrode redox reactions, reducing energy loss during charging, accelerating the charging rate, and simultaneously increasing the energy storage capacity of the electrode[111]. The other is the photo-charging mechanism: photoactive and energy storage components form a synergistic system, which directly converts light energy into chemical energy for storage under illumination, enabling self-charging without an external power supply to meet emergency power demands for low-power flexible electronic devices[112,113]. In both mechanisms, the selection of photoactive components is critical. They must exhibit strong light absorption, high charge-carrier separation efficiency, and good synergy with energy storage components, without compromising the flexibility and electrochemical stability of the device. Photoactive polymers cover various categories such as photoisomerization polymers (photochromic)[114], photocrosslinkable polymers[115], photodegradable polymers[116] and photoconductive polymers. Among them, polyaniline, as a typical photoconductive polymer, exhibits a positive response capability of increased conductivity under almost all excitation light wavelengths, making it an ideal material for photo-enhanced energy storage devices.

Besides the inherent advantage of high specific capacity in batteries, PANI is also an excellent p-type semiconductor[11,117]. In principle, the HOMO–LUMO levels of PANI can be tuned via doping or substituent engineering, enabling the formation of Type-Ⅱ heterojunctions with common photoactive components (e.g., TiO_2, $BiVO_4$, g-C_3N_4). This promotes efficient separation of photogenerated electron–hole pairs, thereby achieving photo-enhanced and even photo-charging performance[118–121].

6.2. Research progress of PANI-based photo-enhanced flexible secondary batteries

Aqueous rechargeable Zn–polymer batteries represent a highly promising alternative to mainstream lithium-ion batteries in terms of cost, safety, and rate performance. However, they suffer from limited specific

capacity and poor environmental adaptability. To address these issues, researchers have successfully utilized ambient air and light to significantly boost the electrochemical performance of aqueous zinc-ion batteries (AZIBs), enable rapid self-charging, and realize switchable multi-mode operation from Zn–polymer to Zn–air batteries. The core of this system lies in an all-in-one polyaniline nanorod array cathode, which possesses reversible redox activity, oxygen reduction reactivity, and photothermal response. The assembled AZIB acts as a highly efficient photo-assisted rechargeable Zn-polymer battery, delivering a remarkable specific capacity of 430.0 mAh g^{-1}. Without an external power supply, the battery can harvest energy from air and light to self-charge within 20 min, releasing a high discharge capacity of 363.1 mAh g^{-1}[122].

Inspired by this research, our group innovatively integrated photo-enhanced batteries with flexible wearable devices. We employed an interpenetrating p–n junction composed of n-type fullerene plasma-induced carbon clusters (FPC) and PANI as the photoelectrode active material, as shown in **Figure 5(a)**. As an electron transport layer, FPC suppresses the recombination of photogenerated electrons and holes in PANI under illumination. The resulting FPC–PANI photoelectrode exhibits an extraordinary 300% photo-enhancement at high charge–discharge rates, with a light-driven capacity of 310 mAh g^{-1} and 91.3% capacity retention after 2000 cycles in **Figure 5(b, c)**. After 10 h of illumination, the synergistic effect between the photocathode and photoanode in the fibrous structure achieves a record photon conversion efficiency of 1.15%. Meanwhile, in **Figure 5(d, e)**, the device maintains excellent flexibility for wearable applications[123].

Polyaniline has achieved breakthrough applications in photo-enhanced aqueous zinc-ion batteries. It not only greatly improves reversible specific capacity and energy utilization efficiency but also enables multi-mode switching between Zn–polymer and Zn–air batteries as well as self-charging without an external power supply. Related studies have further endowed polyaniline-based photo-enhanced batteries with flexibility, achieving both photo-enhanced performance and excellent cycling stability and photon conversion efficiency, meeting the requirements of wearable devices and providing a new approach for the efficient integration of solar energy and electrochemical energy storage. As an emerging research field, photo-enhanced/photo-chargeable batteries still lack an in-depth understanding of the interfacial mechanisms in photoelectrodes and insufficient investigations on performance under complex environments. Nevertheless, with the global promotion of the dual-carbon strategy, energy conservation and environmental protection have become core goals in the energy sector. The efficient conversion of clean energy and integrated photo-electric energy storage technologies are bound to be major research focuses in the future. As a multifunctional material that offers high reversible capacity, acts as a level-tunable p-type semiconductor, and possesses excellent flexibility and processability, PANI will undoubtedly play an increasingly important role in photo-enhanced energy storage devices and become a key material driving the development of next-generation low-carbon, multifunctional integrated energy-storage technologies.

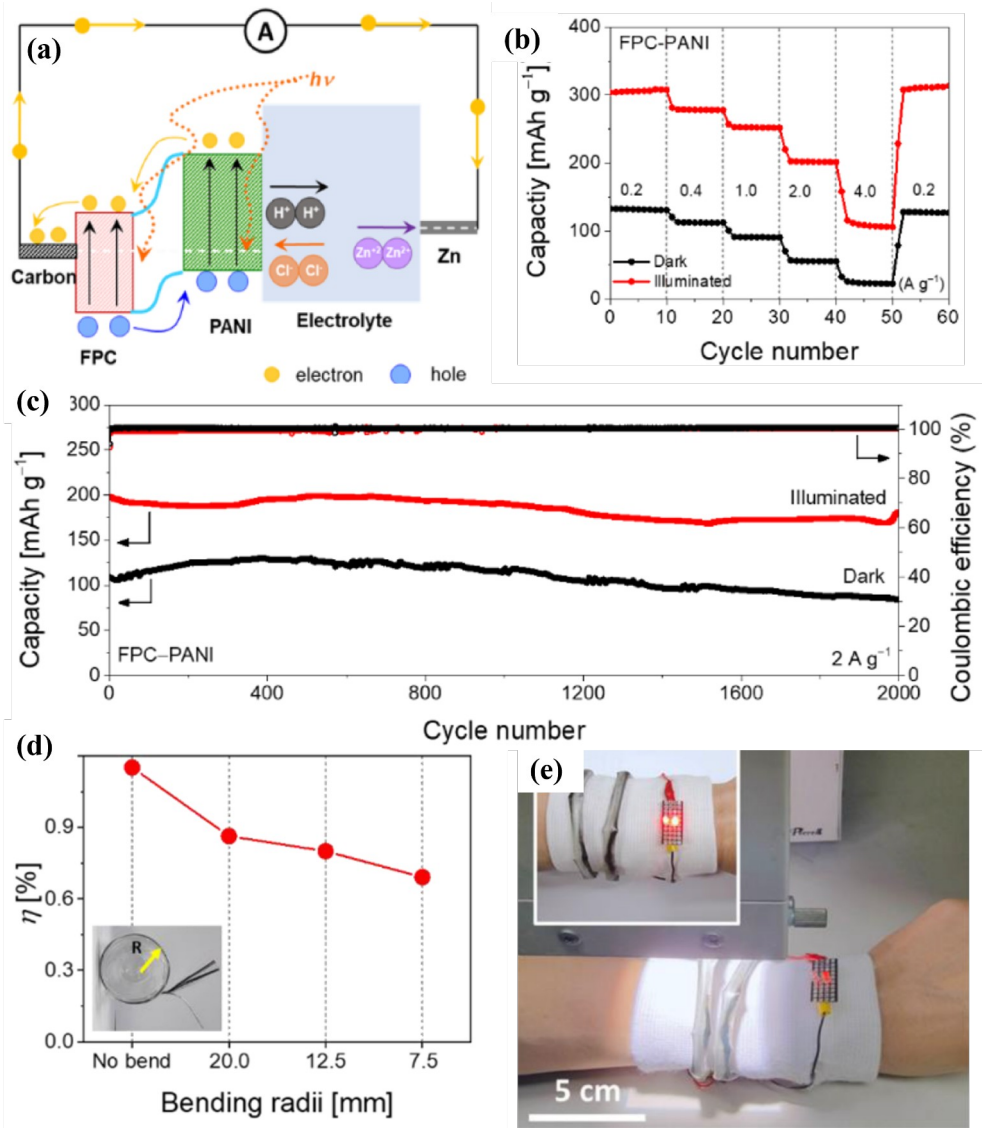

Figure 5. Recent progress in photo-enhanced flexible Zn-PANI batteries: (a) Possible mechanism for the solar charge of battery with FPC–PANI photocathode under illumination, (b) rate capability and (c) cycling performance of solar battery under darkness and illumination, (d) solar charging performances at different bending angles and (e) Images of the fiber-shaped battery powering two LEDs under illumination[123].

7. Summary and perspective

This review systematically summarizes the research status, fundamental mechanisms, current bottlenecks, and optimization strategies of polyaniline (PANI)-based flexible energy storage devices and introduces their extended applications in photo-enhanced flexible energy storage, demonstrating the research evolution and future directions of PANI in the energy storage field.

As a representative conjugated conductive polymer, PANI has become a key electrode material for flexible energy storage devices owing to its abundant precursors, facile synthesis, tunable conductivity, and excellent reversible redox activity. Recent studies on PANI-based flexible devices mainly focus on two systems: flexible supercapacitors and flexible rechargeable batteries. Both rely on composite modification and structural engineering to address the intrinsic drawbacks of pure PANI, including poor mechanical flexibility, severe

volume expansion, and insufficient cycling stability. In flexible supercapacitors, PANI achieves synergistic improvements in flexibility and electrochemical performance by coupling with other functional materials. In flexible rechargeable batteries, PANI plays vital roles in Li-, Na-, and Zn-ion batteries as an active material, conductive coating, or structural reinforcing component. Through electrode modification and device configuration optimization, it effectively enhances capacity, cycling stability, and mechanical endurance. Among these, aqueous zinc-ion batteries represent a particularly important application, where studies have realized simultaneous improvements in electrode mass loading and flexibility.

Although considerable progress has been achieved, PANI-based flexible energy storage devices still face critical challenges, such as electrode pulverization during cycling and weak interfacial adhesion between the electrode and current collector. In response, this work draws on optimization strategies for conventional energy storage devices and proposes three core approaches: molecular doping, nanostructure design, and interface engineering. Furthermore, photo-enhanced flexible energy storage devices are introduced as an emerging direction, aiming to provide new pathways for the development of wearable electrochemical energy-storage devices.

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