

Research Status of Polytriphenylamine-Based Electrode Materials in Electrochromic Supercapacitors

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Abstract

The electrochromic supercapacitor (ECSC) is an emerging device that integrates energy-storage and optical-modulation functions, with its performance fundamentally dependent on the electrode materials. This article systematically reviews the research progress on polytriphenylamine-based electrode materials for ECSCs. It begins by introducing the basic structure and working mechanism of ECSCs, highlighting their high compatibility with conventional supercapacitors in both architecture and operation. Subsequently, the characteristics of three major categories of electrode materials—inorganic compounds, organic small molecules (e.g., viologens), and conductive polymers (e.g., polyaniline, polythiophene, polypyrrole and their derivatives)—are analyzed, with polytriphenylamine-based materials standing out as a research focus owing to their low cost, ease of modification, and tunable optoelectronic properties. The article further outlines the challenges faced by polytriphenylamine materials in ECSCs, such as structural stability, energy-storage density, and limited color-switching range, and proposes performance-optimization strategies including molecular design, bipolar doping, and side-chain engineering. Finally, the application prospects of ECSCs in areas such as energy-saving smart windows and flexible wearable electronics are discussed, emphasizing their significant potential for achieving visual energy management and intelligent human-machine interaction.

Keywords

Electrochromic supercapacitor; Polyphenylene sulfide; Electrode materials; Conductive polymers; Energy storage

1. Introduction

The integration of electrochromic and energy storage functionalities has led to the development of the electrochromic supercapacitor device (ECSC). This type of device combines dual capabilities of electrochromism and electrochemical energy storage: on one hand, it can serve as a smart window, improving indoor photo-thermal comfort by modulating its transmittance; on the other hand, it can also function as an energy storage unit to power small electronic devices such as LED lights and watches. Furthermore, since the color state of the device directly corresponds to its energy storage level, users can visually determine the remaining capacity with the naked eye, thereby avoiding energy waste and device damage caused by overcharging.

2. Electrochromic Supercapacitor

2.1. Structure of Electrochromic Supercapacitor

Electrochromic devices (ECs) and supercapacitors (SCs) share a similar structural design, both featuring a typical "sandwich" layered architecture comprising electrode materials, electrolyte

layers, and conductive substrates (as shown in Figure 1). Due to their high structural similarity, both can be optimized independently through functional layer modifications to construct high-performance integrated devices. More importantly, the core of both ECs and SCs lies in the working electrode, which achieves energy conversion through charge storage and release during redox processes. This shared mechanism provides the material and electrochemical foundation for their functional integration. Additionally, both ECs and SCs can be combined with various novel device forms, such as micro-devices, wearable devices, and implantable devices. Among these three, electrode materials play a decisive role.

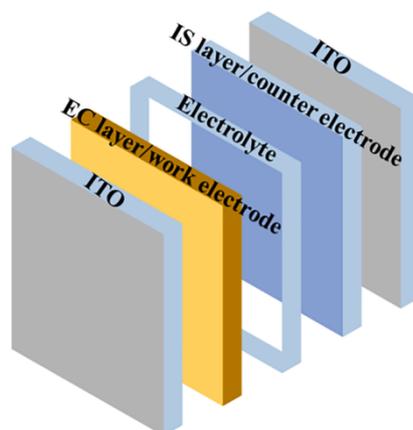


Figure 1: Schematic diagram of electrochromic device and supercapacitor

2.2. Electrochromic electrode materials for supercapacitors

The performance of electrochromic supercapacitors primarily depends on their electrode materials. The surface structure and electronic properties of the electrodes directly influence the efficiency of charge storage and color switching, serving as the key to enhancing the overall reliability and comprehensive performance of the device. Currently, electrode materials applied in this field can be broadly categorized into two main types: inorganic materials and organic materials.

(1) inorganic material

These typically feature metal oxides such as tungsten trioxide (WO_3), vanadium pentoxide (V_2O_5), titanium dioxide (TiO_2), and nickel oxide (NiO) as their core components. Their energy storage mechanism combines the synergistic effects of interfacial electrical double-layer capacitance and bulk pseudo-capacitive effects, thereby achieving high energy storage efficiency. Such materials generally offer good chemical stability (e.g., maintaining over 90% capacity after 2,000 cycles), long cycle life, and high conductivity, making them suitable for long-term stable operation. Particularly, transition metal oxides, benefiting from their compositional diversity and structural tunability, exhibit rapid redox reaction kinetics. Based on their coloring modes, inorganic ECSC materials can be further categorized into anodic, cathodic, and amphoteric types. However, these materials also have notable limitations: due to the slow ion diffusion within inorganic structures, their color-switching response time is relatively long and their energy density is comparatively low. Additionally, their fabrication processes are relatively complex and costly, and most are rigid materials, making it difficult to meet the application demands of flexible electronics for electrochromic supercapacitors.

ELECTROCHROMIC OXIDES:

H																			He
Li	Be											B	C	N	O	F	Ne		
Na	Mg											Al	Si	P	S	Cl	Ar		
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr		
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe		
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn		
Fr	Ra	Ac																	

Cathodic coloration
 Anodic coloration

Figure 2: Electrochromic Elements with Anode and Cathode Coloring Behavior

(2) organic small molecule

A typical example of organic small-molecule electrochromic supercapacitor materials is viologen, which belongs to the class of disubstituted bipyridinium salts and is named for the purple color of its reduced state. The electrochromic process of viologen originates from its reversible transitions among three redox states—namely, the neutral state, the monocation, and the dication—with the reaction pathway illustrated in Figure 3. Its color-switching performance primarily arises from the photo-induced charge transfer effect involving the nitrogen atoms on the pyridine rings. By structurally modifying the substituents on the nitrogen atoms of the pyridine rings or the bridging groups between the bipyridyl units, it is possible to regulate their energy levels, colors, and stability, thereby yielding derivatives with varied properties. However, practical application and development of these materials have long been constrained by issues such as poor stability, inadequate mechanical strength, limited processability, and restricted energy density.

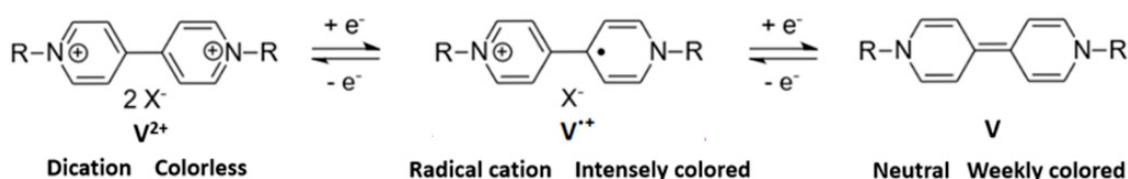


Figure 3: Electrochromic Process of Indigo Naturalis

(3) organic conductive polymer

Conductive polymers, a class of organic macromolecular materials with conjugated π -bond structures, have garnered extensive attention in the field of electrochromic supercapacitors owing to their excellent solution processability, outstanding mechanical flexibility, rich color-switching capability, and tunable band gaps. Among such materials, polyaniline, polythiophene, polypyrrole, and their derivatives currently represent the most widely studied representatives].

(I) PANI

Among various conductive polymers, polyaniline (PANI) and its derivatives integrate efficient electrochemical energy storage with rapid, reversible color-switching capabilities. Polytriphenylamine and its derivatives represent a prominent category within this group.

They offer advantages such as low cost, straightforward synthesis, a wide color-tuning range, good chemical stability, and ease of modification [1]. Consequently, they have emerged as a promising class of materials for electrochromic supercapacitors (ECSCs). According to research by Kanazawa et al., properly designed polytriphenylamine derivatives exhibit reversible color changes within a potential window of 0 V to 1.4 V, with the film color gradually shifting from light yellow-green to cyan.

(II) PTh

As a member of conductive polymers, polythiophene (PTh) and its derivatives have attracted attention due to their easily modifiable structures, tunable bandgaps, and good processability [2]. Their band structures and redox potentials can be flexibly regulated through molecular design, enabling them to deliver considerable pseudo-capacitive energy storage and high optical contrast simultaneously. Coupled with their excellent film-forming ability and potential compatibility with flexible substrate processing, PTh-based materials offer a key material choice for constructing long-lifetime, high-efficiency ECSC devices that meet the demands of flexible electronics. As shown in Figure 4, modified poly(3,4-ethylenedioxythiophene) (PEDOT) exhibits excellent gradient color-switching behavior.

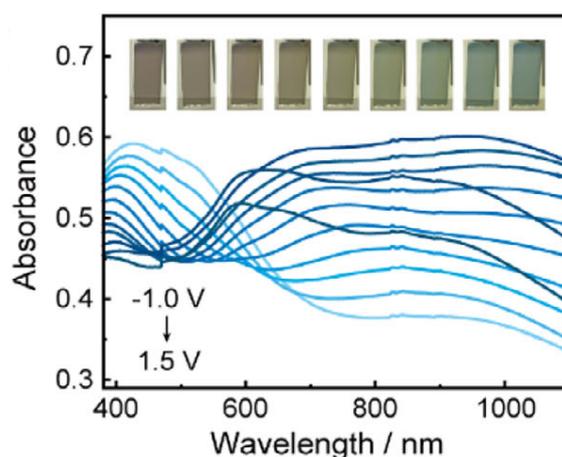


Figure 4: Electrochromic Properties of PEDOT[3]

(III) PPy

Polypyrrole (PPy), a heterocyclic conductive polymer with a conjugated structure [4], has garnered extensive attention in the field of ECSCs owing to its straightforward synthesis, high specific capacitance, and outstanding long-term cycling stability. PPy films exhibit a color shift from yellow to green in the undoped insulating state and from blue to purple in the doped conductive state [5]. Through molecular engineering, an important derivative of PPy—poly(3,4-ethylenedioxyppyrole) (PEDOP)—can be obtained. This material operates at a relatively low voltage, possesses excellent cycling stability and remarkable optical contrast, demonstrating promising application potential.

2.3. Intelligent Application Direction of Electrochromic Supercapacitors

At the critical stage of transitioning from traditional energy storage technologies towards intelligent and multifunctional systems, device design is evolving from a single "energy storage" unit to integrated "storage-feedback-interaction" solutions. As a multifunctional device that combines energy storage with visual feedback, ECSCs have made remarkable progress in the fields of electrochemical energy storage and energy visualization. Its core value lies in the synergistic design of materials and devices, which organically merges the physical process of

energy storage with a visual optical response. This integration thereby creates new possibilities for intuitive information perception and human-machine interaction, demonstrating promising prospects in various emerging fields such as energy-saving smart windows, flexible wearable electronics, self-indicating energy storage systems, and adaptive optical camouflage.

(1) Intelligent Building and Energy-saving Intelligent Window

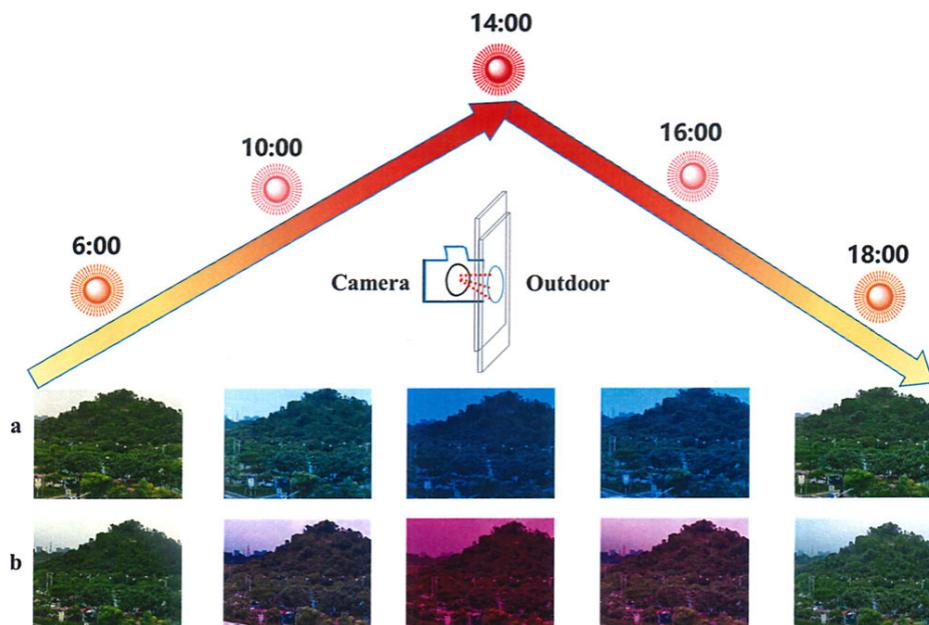
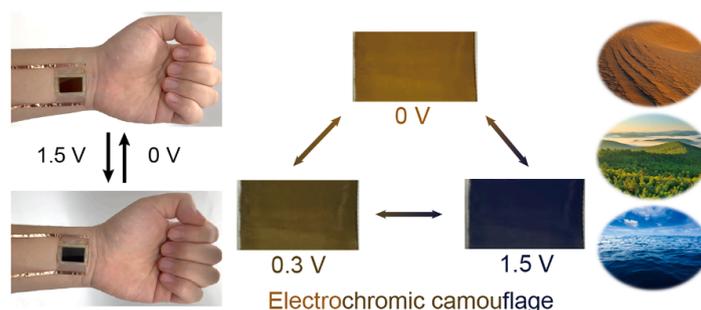


Figure 5: Color Change of Energy-saving Intelligent Window at Different Time[6]

Electrochromic supercapacitors not only enable rapid adjustment of light transmittance for dynamic shading but can also be integrated with power generation units such as solar cells to form self-powered optical regulation systems. This effectively mitigates additional building energy loads caused by window heat loss and solar radiation [7]. When indoor lighting or temperature fluctuates sharply due to external environmental changes, electrochromic supercapacitors can swiftly switch their tinting state based on control signals or adaptive strategies. While modulating natural lighting and thermal insulation performance, they store surplus energy within the device and release it when needed to sustain continuous operation, thereby reducing reliance on the external power grid [8]. As an intelligent energy-optical coupling unit in building envelopes, this device significantly enhances the overall performance of windows in energy saving, light regulation, and energy storage. It promotes the evolution of building windows from passive structural components into active, responsive, and energy-self-sufficient smart systems, offering a feasible technological pathway toward green buildings and low-energy living environments.

(2) Flexible Wearable Electronics

Flexible wearable electronics represent an interdisciplinary frontier that integrates materials science, electronic engineering, biomedicine, and micro-/nano-fabrication technologies. Its core lies in developing flexible/stretchable materials and innovative device architectures to construct electronic systems compatible with the complex curved surfaces and dynamic deformations of the human body. By integrating electrochromic supercapacitors with energy-harvesting units such as triboelectric nanogenerators and flexible solar cells, self-powered intelligent wearable systems can be built, effectively addressing the demand for continuous and lightweight power sources in wearable electronic devices. When changes in the user's motion state, physiological signals, or external environmental stimuli are detected, the electrochromic supercapacitor can swiftly switch its tinting state according to preset programs or biosensor signals. While enabling visual information interaction, health-index feedback, or



adaptive camouflage, it can temporarily store harvested mechanical energy, light energy, etc., within the device and supply power to low-consumption components such as sensors and microprocessors when needed, significantly extending the operational duration of the device. As an intelligent interactive-energy-storage coupling unit in wearable systems, this device can substantially enhance the comprehensive performance of electronic textiles, smart glasses, electronic skins, etc., in terms of information display, personalized decoration, and energy management. It promotes the evolution of wearable devices from single-function accessories into multifunctional, adaptive, and energy-self-sufficient integrated smart systems, offering innovative technological solutions for human-machine interaction, personalized healthcare, military camouflage, and related fields.

Figure 6: The camouflaging scene of wearable device[9]

3. Research Status of Polyphenylene Amine Electrode Materials in Electrochromic Supercapacitors

3.1. Structural characteristics of polyaniline electrode materials

Triphenylamine (TPA) is a propeller-shaped molecule that exhibits good thermal and morphological stability. It is readily oxidized, possesses excellent charge-transport capability, and shows pronounced electrochemical activity and photosensitivity. Due to the high stability of its radical cation, TPA is regarded as an excellent hole-transport material. As a result, TPA-based polymers and their derivatives demonstrate broad application prospects in optoelectronic conductors, light-emitting devices, electrochromic materials, and memory devices.

TPA is colorless in its neutral state, but undergoes a distinct color change upon one-electron oxidation to form a radical cation, accompanied by high optical contrast, giving it significant potential in the field of electrochromism. However, the performance of pure TPA is limited and hardly meets practical requirements. To address this, researchers have introduced TPA into polymer matrices, which not only enhances its properties but also adds further functionality. In 2022, Liou's group[10] successfully synthesized two triphenylamine-based polyamides, TPPA-TB and TPPA-Me-TB, by incorporating Tröger's base (TB). The study found that polymers containing TPA units exhibit faster response speeds during electrochromic switching. Moreover, electrochromic films prepared from such polymers showed excellent cycling stability and reversibility, retaining an optical transmittance contrast above 86% after 500 consecutive cycles. To date, extensive research has been conducted on polytriphenylamine-based materials.

However, the practical application of polytriphenylamine-based materials in ECSCs still faces several key challenges: under high-voltage operating conditions, the material structure is prone to distortion, which compromises cycling stability; its charge-storage capacity requires further

improvement; meanwhile, the relatively limited color response in electrochromic applications also restricts the further advancement of its overall performance. To address these bottlenecks, strategies such as molecular design, structural engineering, and interface optimization can be employed to enhance the comprehensive performance of polytriphenylamine-based electrode materials, thereby meeting the urgent demand for high-performance energy-storage devices in fields like smart wearables and visual energy-storage systems.

3.2. Optimization Strategies for Polyaniline Electrode Materials

Electrode materials are the core determinant of ECSC device performance, as their quality directly dictates the overall device performance. Consequently, enhancing ECSC performance fundamentally relies on improving the materials themselves. Electrical performance is a key metric for these materials, primarily governed by the electronic structure of their conjugated molecules or polymers, as well as intermolecular or interchain π - π interactions and packing arrangements at both microscopic and macroscopic levels. Therefore, the internal molecular structure plays a crucial role in defining charge-transport characteristics.

Performance enhancement can be achieved through molecular design strategies, including:

(1) Modification of triphenylamine and its derivatives: Introducing triphenylamine derivatives with stronger electron-donating ability as structural units into polytriphenylamine-based electrode materials can modulate the electron-cloud density and light-absorption behavior, enhance intramolecular charge transfer, and thereby improve optical performance.

(2) Bipolar doping modification: This approach introduces both p-type and n-type doping active centers into ECSC materials, enabling a single device to store charge over a wider voltage window, which significantly increases its specific capacitance and energy density. The presence of dual doping centers also provides a pathway for achieving multi-color switching or substantially enhancing the contrast of specific color states.

(3) Side-chain modification: By introducing side chains with different electronic effects into the main chain, the electron-cloud distribution of the conjugated system can be regulated, thereby tuning the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels and allowing precise control over optical absorption properties. Meanwhile, the introduction of ion-philic side-chain groups can significantly improve ion affinity, lower the diffusion energy barrier of electrolyte ions, and enhance response speed and rate performance during charging and discharging.

4. Conclusion

Electrochromic supercapacitors (ECSCs), as frontier devices integrating energy storage and optical regulation functions, demonstrate significant potential in smart buildings, flexible wearable electronics, and adaptive camouflage. Polytriphenylamine and its derivatives have attracted considerable attention as electrode materials in this field due to their excellent charge transport properties, tunable optoelectronic performance, and good stability. Through molecular design strategies such as structural modification of the triphenylamine unit, bipolar doping, and side-chain functionalization, the electrochemical energy storage capacity, optical contrast, response speed, and cycling stability of these materials can be effectively enhanced, thereby optimizing the overall performance of ECSCs.

However, polytriphenylamine-based materials still face several challenges in practical applications, including structural distortion under high-voltage operation, limited charge storage capacity, and a relatively narrow range of color responses. Addressing these issues requires further in-depth investigation into the structure-property relationships of the materials, along with advances in interface engineering, composite system construction, and

device structural optimization to promote their integration and application in real-world systems.

Looking ahead, with continuous innovation in material design strategies and gradual maturation of device fabrication processes, polytriphenylamine-based ECSCs are expected to play an increasingly important role in energy visualization, adaptive photothermal management, human-machine interaction, and other related fields. They will provide key material and technological support for the development of next-generation intelligent, self-powered, and multifunctional electronic systems.

References

- [1] Xiao Y, Guntupalli B, Paudyal J. Highly Conductive Porous Paper-Based Metal Thin Films[J], 2016.
- [2] Dai Y Y, Li W J, Zhao R Y, et al. Quadruple thiophene based electrochromic electrodeposited film as high performance hybrid energy storage system[J]. *Electrochimica Acta*, 2019, 318: 322-332.
- [3] Du C, Cheng X, Zhang G, et al. Molecular Bonding Engineering Enables Ultra-Stable Electrochromic Energy Storage in Flexible PEDOT Devices[J], 38.
- [4] A J F, A Y Z, A H Z, et al. Core/sheath structured ultralong MnO_x/PPy nanowires feature improved conductivity and stability for supercapacitor[J], 2020, 559: 39-44.
- [5] Genies E M, Lapkowski M J J O E C, *Electrochemistry I. Spectroelectrochemical study of polyaniline versus potential in the equilibrium state*[J], 1987, 220(1): 67-82.
- [6] Ling H, Wu J, Su F, et al. Automatic light-adjusting electrochromic device powered by perovskite solar cell[J], 2021, 12(1): 1010.
- [7] Li G, Jiang X, Asfahan H, et al. Humidity-Controlled Smart Window with Synchronous Solar and Thermal Radiation Regulation[J], 2025, 000(000).
- [8] Sun F, Pal R, Eom S Y, et al. Fast-switching dual-cathode electrochromic smart windows for year-round building energy savings[J], 2025, 16(1).
- [9] Du C, Cheng X, Lu B, et al. Engineering a 3D conductive polythiophene network with conformational locking for camouflaged wearable electrochromic-supercapacitor devices[J], 2010, 80(000): 9.
- [10] Hsiao S H, Liao W K, Liou G S. A comparative study of redox-active, ambipolar electrochromic triphenylamine-based polyimides prepared by electrochemical polymerization and conventional polycondensation methods[J]. *Polymer Chemistry*, 2018, 9(2): 236-248.