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Use electrochemistry to charge the next dynamic thermal metamaterials

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ABSTRACT

Electrochemistry has enabled a wide range of important energy technologies such as fuel cells and batteries, emerging as a powerful tool to achieve active materials and devices with novel applications. In this Perspective, we highlight the great potential of electrochemistry in propelling the next generation of dynamic thermal metamaterials with a focus on thermal radiation applications. After a brief introduction of the mechanisms of electrochemistry to change material properties, we discuss the possibilities of achieving highly tunable thermal radiation features by electrochemically manipulating the carrier densities of plasmonic materials. Recent studies in the intersections between electrochemistry, metamaterials, and thermal radiation applications are reviewed, indicating an emerging research direction incorporating these three fields — electrochemically dynamic thermal metamaterials. Towards this direction, we anticipate a promising pathway of employing conducting polymers and point out its remarkable opportunities and potential challenges. We hope this perspective could encourage more researchers to contribute to the development of this interdisciplinary field targeting the next energy technologies and applications.

The science of electrochemistry deals with the relationship between electrical and chemical energy, demonstrating the ability to change materials at the molecular level with an electric current or, reversely, generate electricity via chemical reactions [1]. With this characteristic, electrochemistry has revealed its enormous potential in energy conversion, storage, transportation, and utilization, as manifested in many important technologies, including fuel cells [2,3], batteries [4,5], water splitting [6,7], carbon dioxide reduction [8,9], and low-grade heat harvesting [10]. One of the main reasons that electrochemistry has become so essential is the impinging need for electrification [11,12], replacing the carbon-intensive fossil fuel-driven processes with renewable energy such as solar radiation and wind. In addition, electrochemistry has enabled a wide range of active materials with substantial tunability and reversibility [13–18], opening up new possibilities for manipulating heat transfer with dynamic thermal metamaterials [19].

The research of metamaterials stems from the pioneering works on optics pursuing exotic phenomena such as negative refraction [20–22] and has subsequently inspired the fast development of a new branch of thermal science — thermal metamaterials [23–25]. With the well-designed artificial structures, thermal metamaterials have demonstrated great capability in the manipulation and utilization of thermal energy for all the three forms of heat transfer: conduction, convection, and radiation [19]. To date, thermal metamaterials have greatly empowered many intriguing applications including thermal cloak [26], illusion [27], and diode [28]. These thermal metamaterials, once incorporating electrochemically active elements, can be upgraded with highly variable thermal conductivity (κ), convective heat transfer coefficient (h), and emissivity (ε) as a function of the applied bias, E (Fig. 1). In the past decades, although electrochemistry has led to many appealing dynamic thermal devices such as thermal transistors [29], its application in thermal metamaterials is still largely untapped. In this Perspective, we discuss the great potential of this emerging field with a focus on the thermal radiation applications.

Electrochemistry uses electrons from the external circuit to tune the material and ions from the electrolyte to achieve charge neutrality. Decoupling of electrons and ions reaction pathways allows extremely fine control of the materials' chemical potential (i.e., the Fermi level) conveniently using electronics. The exact end state after Fermi level tuning depends on the materials and ion species, which can be generalized into four mechanisms: capacitive charging, surface redox reaction, ion insertion, and electrodeposition (Fig. 2a) [30–33]. The first two mechanisms modify the surface characteristics of materials, and the latter two aim at achieving a complete change or creating a new material layer. These differences enable a variety of spatiotemporal material

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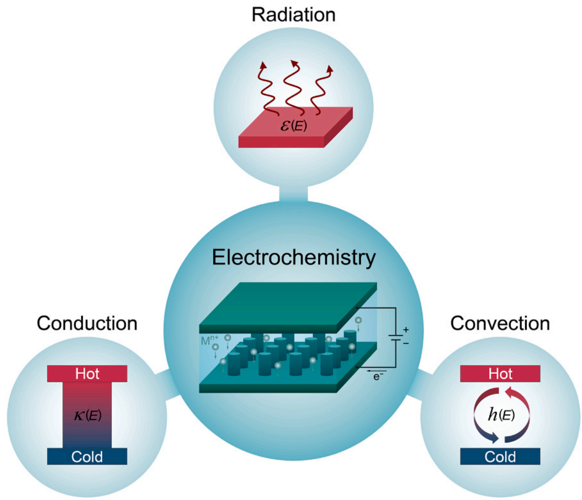

Fig. 1. Electrochemically dynamic thermal metamaterials.

tunability for desirable applications [34–36].

With the ability to manipulate Fermi levels, electrochemistry is especially useful in designing functional plasmonic materials to tailor light-matter interactions by changing their free carrier densities [37]. Many unique properties of plasmonic materials originate from the resonance between the electromagnetic waves and the collective oscillation of free carriers. Such resonance can generate a large density of states in the vicinity of plasmonic materials, capable of greatly enhancing the light trapping and shaping the absorption/emission spectrum [38]. This ability has been successfully applied to a wide range of advanced technologies such as photothermal therapies [39,40], solar energy harvesting [41,42], thermophotovoltaics [43,44], and radiative cooling [45–49]. Typical plasmonic materials include noble metals, metal oxides, semiconductors, and conducting polymers, with the resonant wavelengths (i.e., plasma wavelength) covering a broad spectrum ranging from ultraviolet to infrared (Fig. 2b). By electrochemically tuning the carrier density (n_c) of these materials, the plasma wavelength (λ_p) can be shifted generally following a trend of $\lambda_p \sim (n_c)^{-\frac{1}{2}}$ [38], which provides an extraordinary opportunity in tuning thermal radiation. This potential is even greater when it comes to electrodeposition where metals are created and effectively "replace" the electrolyte, leading to dramatic changes in the optical properties. For example, reversible metal electrodeposition can create/dissolve a metal layer (e.g., Ag) on top of the electrolyte and switch the device between highly reflective ($\varepsilon \approx 0$) and emissive ($\varepsilon \approx 1$) with a near-unity contrast of mid-infrared (mid-IR) emissivity [50–52]. In this way, electrochemistry could greatly empower many emerging thermal applications including infrared camouflage [53], personal thermoregulation [54,55], smart windows [56], and net-zero-energy buildings [52] (Fig. 2c).

As the only way of heat transfer between the Earth and the surrounding universe, thermal radiation plays a key role in addressing the global warming issue with the hope to fully control the heat either received from the extraterrestrial heat source (the Sun, ~5800 K [73]) or released to the heat sink (the deep space, ~3 K [74]). It is therefore essential to develop the ability to regulate thermal radiation, and electrochemistry has made significant contributions (Fig. 3a). As an example, electrochromic smart windows with actively tunable optical properties over visible and infrared spectrums considerably reduce the energy consumption for indoor heating and cooling [15,75,76]. The fact that buildings consume as much as 40% of global energy has demanded tremendous efforts in developing electrochromic windows for energy-efficient buildings during the past decades [77–83]. These nontrivial efforts lead to a variety of high-performance smart windows with substantial optical modulation, fast response, long-term durability, large functioning area, high flexibility, multiband capability, and scalability. In 2017, Barile and McGehee et al. utilized reversible metal electrodeposition to achieve large contrast and color-neutral dynamic windows [78]. Separate multispectral control was also realized in 2013 by Milliron's research group using metal oxides with different tuning potentials and optical conductivities [77]. It is worth mentioning that the electrochromic devices based on either metal electrodeposition [84] or capacitive charging of metal oxides [58] have been demonstrated with excellent stability even after 10,000 switching cycles. Despite these exciting achievements, significant electrochromic effects are mainly limited to visible and near-infrared regions, and the mid-IR tunability remains largely underexplored. To address this challenge, in 2023, Sui et al. [52] developed an electrochromic design with a substantial mid-IR emissivity contrast of 0.85 via reversible metal electrodeposition, suggesting a promising pathway towards net-zero energy buildings. In addition to the thermal regulation of buildings, electrochemistry also finds important applications in personal thermal management [85–87]. Chen et al. [88] demonstrated a wearable variable-emittance (WeaVE) device capable of dynamically tuning the thermal radiation heat loss of human body in response to ambient temperature changes. This was enabled by actively controlling the free carrier density in polyaniline. As

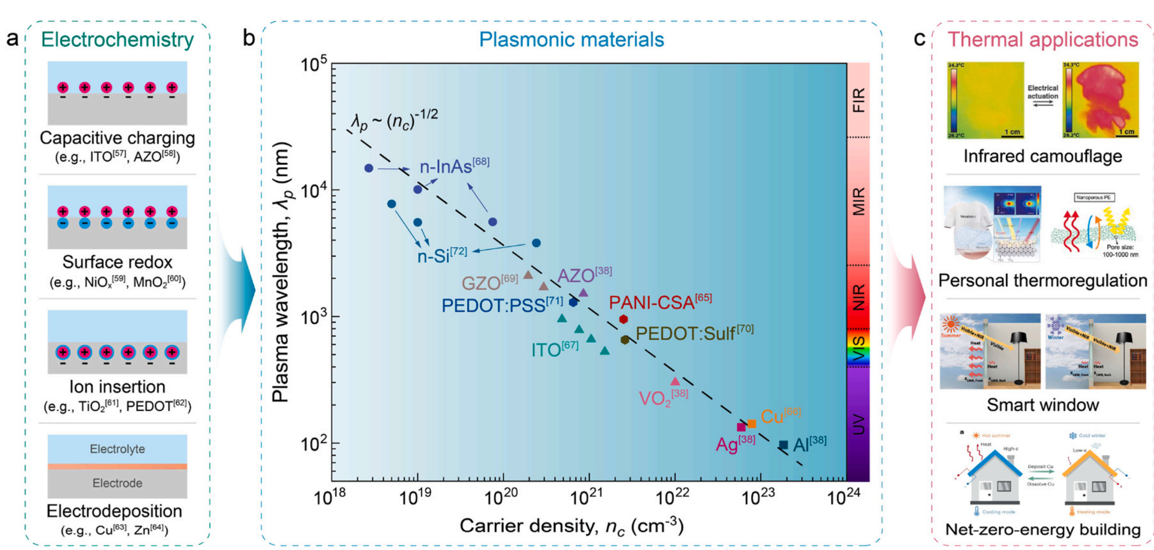

Fig. 2. Mechanisms and applications of electrochemically tunable plasmonic materials. (a) Four electrochemical mechanisms for controlling material properties [57–64]. (b) Carrier density and plasma wavelength for various plasmonic materials [38,65–72]. (c) Representative emerging thermal applications [52–56].

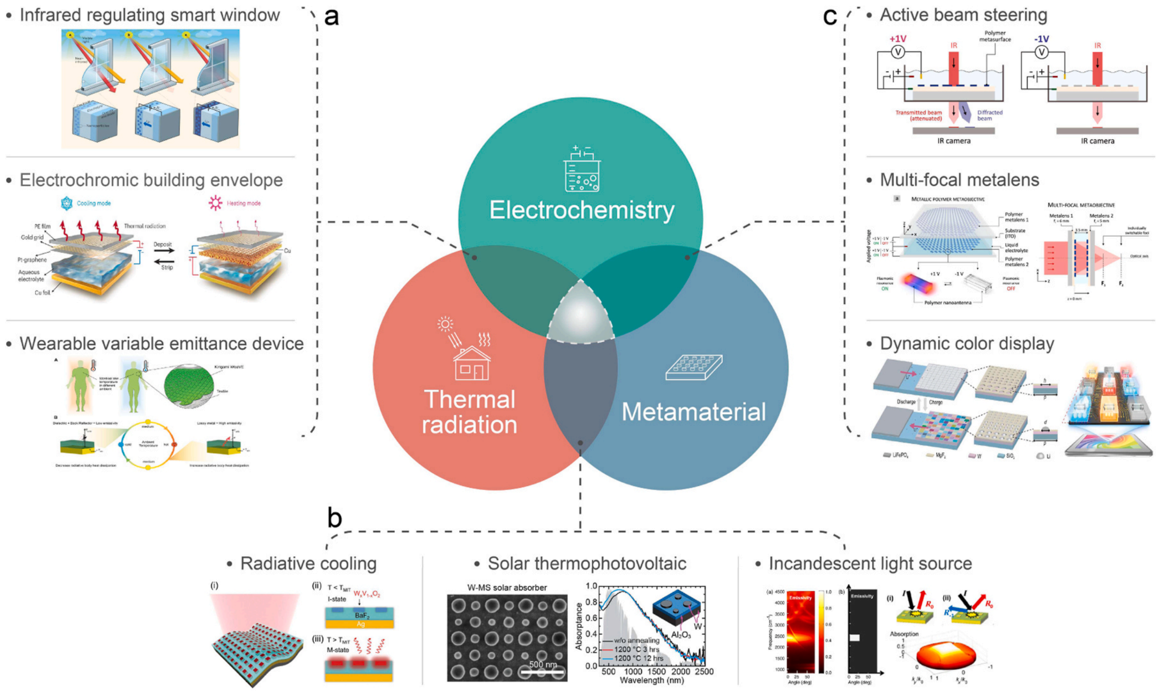

Fig. 3. Intersections and applications of electrochemistry, thermal radiation, and metamaterial. (a) Applications of electrochemistry-mediated thermal radiation [52,88,121]. (b) Applications of thermal metamaterials [100–102]. (c) Applications of electrochemically tunable metamaterials [71,119,120].

a result, WeaVE achieved a 4.9 ℃ expansion of thermal comfort zone — equivalent to a continuous power input of 33.9 W/m^2, upon an energy cost as low as 55.8 J/m^2 per switching. These examples have shown the great ability of electrochemistry in manipulating the responses to solar radiation and regulating the thermal emission, with a leverage of its broadband tunability throughout the visible and infrared regimes. Another advantage of electrochemistry as a controlling approach is the compact form factor for device miniaturization in conjunction with low cost and long durability, compared to other advanced thermal designs requiring moving parts and mechanical actuation systems [89–91].

The journey towards better efficiency, tuning range, and functionality continues for electrochemically tunable optical materials, and one shall ask the question – what is next? Thanks to the advancement of nanofabrication technology in the past decades, numerous subwavelength-structured metamaterials with many exotic properties have been created [19,92]. By leveraging rationally designed nanostructures, metamaterials and their two-dimensional counterparts, metasurfaces [93,94], allow an elaborate control of light-matter interactions. In 2021, Overvig et al. [95] theoretically pointed out the potential of metasurfaces in achieving a full control of thermal radiation in terms of spectrum, polarization, and directionality. Such potential has successively been revealed in a plethora of inspiring experiments [96–99], and has facilitated many advanced thermal applications such as self-adaptive radiative cooling [100], solar thermophotovoltaics [101], and incandescent light sources [102] (Fig. 3b).

For thermal radiation applications, introducing subwavelength structures opens up a new design dimension for achieving unique spectral and angular profiles, which can overcome many limitations in the thin-film configuration. Taking dynamic radiative cooling as an example, though reversible electrodeposition has proven substantial mid-IR tunability, generating a metal film also significantly blocks the visible light, making it impossible to realize a transparent thermal regulator for window applications [58]. This limitation can potentially be overcome by employing metamaterials with specially designed resonating nanostructures. Therefore, the delicate control of thermal radiation enabled by electrochemical metamaterials is of great value for applications such as advanced infrared camouflage [103–106], nonreciprocal absorption [107,108], and directional thermal emission [109].

The potential of electrochemical metamaterials in tuning thermal radiation, regarding its physical essence of electromagnetic wave, is manifested in the successful application of electrochemistry for dynamic optical metamaterials [110–112]. The unique optical features of metamaterials usually arise from local resonances around the nanostructures, making them highly sensitive to the surrounding material properties. Such sensitivity is particularly desirable for electrochemistry to yield significant tunability. Within the past few years, we have witnessed many impressive advancements of electrochemically dynamic optics showcasing high performance and novel functions [113–118]. For example, Karst et al. [71] realized electrochemically tunable metasurfaces for active beam steering with a video-rate switching speed and a 100% contrast ratio of transmission intensity. Other appealing cases demonstrated recently include multi-focal metalens [119] and dynamic color display [120] (Fig. 3c). These advancements in optical devices indicate a promising future of applying electrochemistry in active thermal metamaterials that target infrared wavelengths.

One intriguing way to achieve electrochemically tunable thermal metamaterials is to utilize conducting polymers (CPs) — organic materials with DC conductivity as high as >1000 S/cm [65,122,123]. This conductivity can be tuned dynamically by controlling the chemical doping level and the free carrier concentration, and is directly related to the modulation of optical and radiative properties [124,125]. A powerful strategy for generating the electrochromic performance of CPs is to apply electrochemical potential and drive the diffusion of dopants between the electrolyte and the CP matrix [125]. Accordingly, CPs can continuously be switched between plasmonic and insulating materials, offering a large tunable space of complex refractive indices. Ranging from nanoantennas [70,126] to beam-steering devices [71,117] to structural colors [127,128], CPs have shown substantial impacts by transforming static devices into their dynamic counterparts. This capability of CPs has also been utilized to control the thermal radiation by leveraging their electrochemically tunable mid-IR emissivity and enables many variable-emittance devices [88,129,130]. Nevertheless, the realization of high-performance dynamic thermal metamaterials based on CPs is still considerably challenging.

From an optical point of view, it would be desirable if CPs can distinctively be switched from a reflective metallic state to a transmissive insulating state. Such a metal-to-insulator transition, which could yield substantial optical contrast, is especially useful in manipulating thermal radiation and has led to many appealing applications [100,131,132]. However, in the mid-IR region, CPs are usually lossy and feature large optical extinction either in metallic or insulating states [133], which is unfavorable in terms of the accessible optical contrast. Specifically, the lossy feature of CPs largely limits their tunability in the mid-IR emissivity as it is hard to eliminate the intrinsic emission of CPs when trying to "turn off" the thermal radiation. To address this challenge, one solution is to further increase the conductivity by controlling the microstructures and charge transport properties synthetically [134–141]. While certain processes can be beneficial to the conductivity, it is worth noticing that the electrochromic properties of CPs depend not only on their conductivity but also on structures and kinetics [142–146]. Studies suggest that CPs experience asymmetrical relaxation and contraction during the redox reaction, which may result in a long switching time and unreliable performance [147–150]. More in-depth explorations on the kinetic correlation between charge transport, structural evolution, and optical contrast in CPs are needed to improve their electrochromic performance. Another challenge lies in minimalizing the side effects caused by the accessories of CPs-based devices — the electrolyte and electrodes. They are necessary for electrochemically biasing the CPs to realize dynamic functions. Nevertheless, they are usually accompanied by undesired infrared absorption which limits the accessible tunability of thermoregulation devices. To address this issue, two-dimensional materials such as graphene are promising candidates of transparent electrodes [50,52], while the desired low-absorption electrolyte is still largely elusive.

To conclude, the utilization of electrochemistry in thermal metamaterials is appealing yet largely untapped to date. This interdisciplinary field calls for efforts in terms of fundamental theories (optics, electrochemistry, and materials science), polymer synthesis, device physics, advanced characterization techniques, and integrated application-driven engineering. Regarding the achievements of its predecessors in optics, we expect the thriving and flourishing of electrochemically dynamic thermal metamaterials in the near future.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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