## Industrial Chemistry & Materials

## REVIEW

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## 1 Introduction

The evolution of industrial development has been characterized by a series of revolutionary breakthroughs. Commencing with mechanized production and progressing through the ages of electrification and mass automation, these paradigm shifts have profoundly redefined productivity paradigms, societal frameworks, and the global economic landscape. In the current era, the synergistic integration of digital technologies, intelligent systems, and cyber-physical interfaces is catalyzing a new phase of technological convergence. Transcending conventional efficiency and automation, the modern industrial paradigm advocates for a symbiotic human-machine coevolution, with heightened emphasis on sustainability, systemic resilience, and corporate social responsibility. This



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Electronic information materials (EIMs) are key enablers for building a smart society. As the material carriers of next-generation information technology, the development of EIMs is increasingly constrained by the challenges of manufacturing precision, heterogeneous integration reliability, and circular economy compatibility. As traditional approaches struggle to meet the demands for nanoscale machining, low power consumption, structural flexibility, and environmental compatibility, there is an urgent need for disruptive materials and methodologies. Ionic liquids (ILs), with their unique combination of tunable molecular structures, negligible volatility, broad electrochemical windows, and strong solvation capabilities, offer a promising route to address these bottlenecks. As dynamic reaction media, ILs precisely regulate the nucleation kinetics and interfacial behaviours of zero dimension (0D) guantum dots, one dimension (1D) nanowires, and two dimension (2D) semiconductors through their unique solvation environments, yielding advanced materials with next-generation EIMs. Leveraging hydrogen bonding and ion-exchange interactions, ILs enable selective extraction and recycling of critical electronic chemicals (e.g., rare earth elements, conductive polymers), offering greener alternatives to conventional solvent-based processes. In field-effect transistors and flexible electronics, ILs improve charge transport efficiency, reduce operating voltages, and enhance interfacial stability, while their compatibility with heterogeneous integration addresses reliability challenges in scalable manufacturing. This review systematically examines ILs roles in advancing EIMs and proposes design principles for their targeted application, highlighting their potential to drive sustainable innovation in electronic materials science.



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paradigm shift represents not merely an intensification of digital transformation, but rather a fundamental reorientation toward innovations that harmonize cutting-edge technological sophistication with human-centric design principles.<sup>1</sup> Within this broader context of technological transformation, the electronic chemicals (ECs) industry is assuming an increasingly pivotal role.<sup>2,3</sup> As specialized fine chemicals essential to the modern electronics industry, ECs are foundational to the fabrication of integrated circuits, flat-panel displays, photovoltaic devices, and a variety of emerging technologies. Functioning as a critical interface between fundamental scientific inquiry and industrial-scale application (Fig. 1), ECs not only enable but also accelerate material and device innovation.<sup>4,5</sup>

However, the accelerated advancement of electronic information technologies, propelling by 5G communications, artificial intelligence (AI), cloud computing, the Internet of Things, and smart devices, has imposed increasingly stringent requirements on the properties, performance, and reliability of next-generation electronic materials. Although considerable progress has been achieved, several critical challenges persist in this field. First, the dual imperatives of material innovation and environmental sustainability have become paramount. There is an urgent need to develop novel functional materials that not only exhibit superior performance but also demonstrate eco-compatibility, aiming to replace conventional silicon-based systems. Second, ultrahigh chemical purity (e.g.,  $\geq 99.9999\%$  for semiconductorgrade chemicals) has emerged as an essential criterion, as even trace impurities can significantly degrade device performance and yield. Third, the escalating complexity and integration density of modern electronic devices (e.g., 3D Integrated Circuit, heterogeneous integration packages) necessitate highly tailored chemical formulations with exceptional compatibility, process-specific functionality, and long-term operational stability. These multifaceted demands

have exposed the limitations of traditional material systems, driving the exploration of adaptable, tunable, and multifunctional chemical platforms (*e.g.*, ILs, MOFs, and organic–inorganic hybrids) to meet next-generation technological requirements.

In this context, ILs, a class of thermally stable, nonvolatile, and structurally tunable solvents composed entirely of ions, have emerged as promising alternatives. Their inherent properties, including exceptional electrochemical stability,<sup>6</sup> low volatility,<sup>7</sup> superb thermal stability,<sup>8</sup> and high level of customizability,<sup>9,10</sup> make them particularly attractive for advanced material processing. Beyond bulk properties, ILs can create unique microenvironments *via* specific solutesolvent interactions, such as dipolar interactions, charge delocalization, hydrogen bonding, and Lewis acid/base behaviour, that enable precise control over reaction kinetics and interfacial phenomena.<sup>11–13</sup> These capabilities have already been widely exploited in other domains of materials science, including catalysis, nanomaterial synthesis, battery electrolytes, and separation science.<sup>14</sup>

Despite their success in adjacent fields, the application of ILs in EIMs remains relatively nascent. To date, few systematic studies have addressed how ILs can be strategically leveraged to meet the evolving demands of the ECs industry. This represents both a critical research gap and a significant opportunity. In this review, we aim to bridge this gap by critically examining the physicochemical features of ILs in the context of ECs design and exploring their functional roles in three core areas, EIMs, separation and purification, electronic devices. By analyzing representative case studies and distilling the underlying mechanisms by which ILs exert influence, we propose conceptual frameworks to guide the rational design of IL-assisted ECs. We believe that a deeper understanding of IL-material interactions will facilitate the development of next-generation EIMs with superior performance, precision, and sustainability.

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Excellent Young Scholars" in 2022. Prof. Liu mainly engages in the design of catalysts, and technology for synthesis of oxygencontaining high-value chemicals and electronic chemicals.

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### 2 Properties of ILs in EIMs

#### 2.1 Design guidelines for EIMs

Contemporary industrial innovation is undergoing a strategic transition from single technology breakthroughs to a systemic convergence paradigm, which is particularly noticeable in the field of EIMs. In order to break through the high-performance computing demands of von Neumann architectures, material design must go beyond the physical limits of silicon-based systems to address data bottlenecks, high energy consumption and latency challenges with multi-dimensional <u>co-</u> innovation.<sup>15–17</sup> In order to achieve this objective, it is necessary to enhance the efficiency-orientation of first-generation EIMs, thereby transitioning to a systemic design philosophy that integrates quantum modulation, dynamic interface engineering and sustainable manufacturing.<sup>18,19</sup> In this section, the design guidelines for EIMs under the technology convergence paradigm are systematically elaborated, based on the requirements of this paradigm shift. These guidelines are derived from three dimensions of electronic structure design, carrier transport optimisation and interfacial physicochemical engineering, based on energy band theory, transport physics and interface science. The central role of ILs as a tool for dynamical regulation is demonstrated.

Energy band theory, a cornerstone of condensed matter physics, reveals the microscopic mechanisms underlying the electrical conductivity, optical properties and magnetic properties of materials. Its core lies in the distribution laws of electrons in the allowed and forbidden bands (e.g., Fermi energy level positions, band gap widths, carrier effective masses).20,21 Dynamic fine-tuning of the energy band structure has become a key challenge in order to achieve precise design of macroscopic physical properties of electronic information materials. The development of ionic liquid gating (ILG) technology, based on the unique electrochemical properties of ILs, is one of the frontiers for achieving "in situ editing" of energy bands.<sup>22</sup> In 2007, Frisbie group's reported the first double-dielectric layer (EDL) using an ILs as the gate dielectric, with a mobility increase of up to 3 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> for a rubbery conventional SiO<sub>2</sub> gate.<sup>23</sup> The basic principle of ionic liquid gating technology stems from the EDL, *i.e.* the formation of a EDL structure between the ILs and the surface of the material (Fig. 2a). In this structure, the EDL effect formed by the cations and anions of the IL is capable of inducing carrier density changes up to the order of 10<sup>14</sup> cm<sup>-2</sup> at the material surface through the construction of a localised electric field modulated by the energy band structure. In contrast to conventional solid oxide gate dielectrics, ILs precisely control the electronic states of materials by dynamically tuning the electric field distribution, especially in two-dimensional materials, where metal-insulator transitions can be dynamically induced or tunable carrier types can be achieved by ionic liquid gating.<sup>24</sup>

In the development of high-performance functional devices, the energy levels of molecules with quantum interference effects can be tuned to an anti-resonance state by gate electrode potentials gated by ILs.<sup>18</sup> This allows direct observation of sharp destructive quantum interference (DQI) properties due to changes in the relative positions of molecular energy levels. For example, the DQI effect of mesophenyl molecules with

V<sub>G</sub> = 1.5 V

Gate

IL-treated

IL-treated

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HRS-4



**Fig. 2** Design principles for electronic materials under technology integration. (a) ILG based on band engineering;<sup>28</sup> (b) green perovskite LED *via* carrier strategy;<sup>29</sup> (c) hetero-structured MoTe<sub>2</sub> for hydrogen evolution reaction enabled by interface design.<sup>30</sup> Copyright 2021, MDPI; 2024, Elsevier and 2024, ACS.

dihydrobenzo[*b*]thiophene as an anchoring group (*meta*-BT) can be controlled by the electrode potential of 1-butyl-3methylimidazolium hexafluorophosphate [Bmim][PF<sub>6</sub>].<sup>25</sup> At a gate potential of -0.4 V, the molecular conductivity is two orders of magnitude lower than at a gate potential of 0 V, which is mainly due to the DQI effect. Similarly, the junction of 2,4-TP-SAc with DQI can be controlled by the ionic liquid gate.<sup>26</sup> The conductance of the molecular junction decreases and then increases in the potential ranges of -0.6 V to -0.4 V (with respect to Ag/AgCl) and -0.4 V to 1.4 V (with respect to Ag/AgCl), resulting in on-off ratios of up to  $\sim 100$  times higher. This demonstrates the feasibility of constructing high-performance single-molecule devices by continuously and efficiently modulating molecules with the DQI effect through ILs. In addition to individual molecules, the monomolecular layer formed by molecular self-assembly also has the same quantum interference effect as the basic molecules, which is conducive to the construction of efficient and stable quantum tunnelling field effect devices. For example, a vertical molecular tunneling field effect device with an ILG was created using pseudo-*p*-bis ((4-(acetylthio)phenyl)ethynyl)-*p*-(2,2) cyclohexane (PCP) together with DQI to achieve ~330 on–off current ratio.<sup>27</sup> In addition to quantum interference effects, the creation of high-performance single-molecule functional devices can be achieved by combining various molecular properties with ILG control. When the structure of the single-molecule junction is fixed, the enhanced molecular electric field response allows for larger switching ratios at lower gate voltages. This is due to the fact

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that molecules containing azulene centres have higher dipole moments, resulting in lower leakage currents (currents when the Fermi energy level is between the HOMO and LUMO orbitals). Therefore, this increases the on/off ratio.

In electronic and optoelectronic devices of the next generation, carrier scattering has been shown a significant effect on device performance.<sup>31</sup> To this end, researchers have proposed various strategies, such as introducing 2D materials (e.g., graphene, h-BN) to construct van der Waals heterostructures, strain modulation, and surface passivation methods to suppress interfacial states and scattering phenomena.32,33 In hetero-structured semiconductors, synergistic effects such as interfacial charge transfer, band alignment and spin orbit coupling play a decisive role in the transport performance of devices.<sup>34</sup> By accurately designing these interfacial behaviours, not only can carrier complexation be effectively suppressed and scattering be reduced, but also ideal energy band structures and transport channels can be constructed to support the development of cutting-edge applications such as spintronics and valleytronic applications. It is noteworthy that interfacial engineering strategies based on ILs offer more efficient solutions to the aforementioned processes. For instance, in the context of chalcogenide lightemitting diodes (LED), the use of 1-butyl-3-methylimidazolium  $([Bmim][BF_4])$ tetrafluoroborate and 1-benzyl-3methylimidazolium tetrafluoroborate ([Bzim][BF4]) has been demonstrated to facilitate the efficient passivation of surface trap defects through the establishment of hydrogen bonds. This process is concomitant with the modulation of the Fermi energy level of the chalcogenide, thereby ensuring its positioning at the mid-band level. This, in turn, has been shown to result in a substantial enhancement in device performance. The mid-band position has been shown to significantly enhance the performance of the device. The ILs-treated chalcogenide material has been demonstrated to achieve an external quantum efficiency of up to 20.03%, and the prepared Pe LED have exhibited green and efficient luminescence with a brightness of up to 57599.36 cd  $m^{-2}$  (Fig. 2b).<sup>29</sup>

The advent of a new generation of EIMs, characterised by heterogeneous integration, has given rise to a series of challenges that have heretofore not been encountered. These challenges are manifest in the interface multidimensional structure of devices.<sup>30,35</sup> As previously stated, ILs demonstrate distinctive advantages in the modulation of interfacial electronic structure due to their high designability. Recent studies have demonstrated that an IL-system comprising an organic superbase and bis(trifluoromethanesulfonyl)imide (TFSI) can be utilised for the electrochemical doping of carbon nanotubes (CNTs), thereby achieving excellent n-type and p-type doping stability (Fig. 2c). The system has been demonstrated to effectively regulate the Seebeck coefficient and conductivity by adjusting the polarity and amplitude of the applied potential. Furthermore, it has been shown to achieve reversible adjustment of thermoelectric properties in a wide range, and to exhibit a stable operation capability of more than 1500 h at an operating temperature of 100 °C.<sup>36</sup>

More critically, EDL effect induced by ILs significantly enhances the thermoelectric properties of the doped films. Under n-type (-0.25 V vs. Ag/Ag<sup>+</sup>) and p-type (+1.5 V vs. Ag/Ag<sup>+</sup>) bias, the resulting CNTs films achieved 104  $\mu$ W m<sup>-1</sup> K<sup>-2</sup> and 223  $\mu$ W m<sup>-1</sup> K<sup>-2</sup> power factors, which are close to the highest levels of thermoelectric CNTs in the literature.<sup>37,38</sup> This suggests that ILs can not only achieve efficient carrier modulation at the interface, but also effectively enhance the performance limit of thermoelectric materials.

As discussed above, the development of next-generation EIMs requires a holistic design strategy encompassing electronic band engineering, carrier transport enhancement, and precise interfacial modulation. ILs have demonstrated unique advantages in each of these domains by enabling non-invasive, reversible, and highly localized tuning of material properties. Their integration into material systems across different spatial dimensions (0D to 2D) reveals significant potential to overcome long-standing limitations in electronic material performance.<sup>39</sup> In the following section, we systematically examine how ionic liquids contribute to the performance of electronic information materials across different dimensional regimes, highlighting their role as dynamic enablers of functional enhancement and design flexibility.

#### 2.2 ILs as tunable platforms for EIMs

ILs are generally defined as salts composed entirely of ions, which remain liquid below 100 °C, a criterion that distinguishes them from conventional molten salts.<sup>40</sup> Their modular structure enables the independent selection and combination of a wide array of organic cations (e.g., imidazolium, pyridinium, phosphonium) and organic/inorganic anions (e.g., [TFSI], [BF<sub>4</sub>],  $[PF_6]$ ), giving rise to a virtually limitless chemical space (up to 10<sup>18</sup> theoretical combinations). This structural diversity is exemplified by aprotic ILs containing large cations (e.g., imidazolium, pyridinium, phosphonium) paired with compact anions, commonly inorganic species ([Br]<sup>-</sup>, [Cl]<sup>-</sup>, [PF<sub>6</sub>]<sup>-</sup>, [BF<sub>4</sub>]<sup>-</sup>) or organic counterparts like TFSI (Fig. 3a).41 In contrast, protic ILs derive from proton transfer between Brønsted acids and bases, creating proton-donor/acceptor sites that enable hydrogen-bonded networks.<sup>42,43</sup> This structural flexibility underpins their core advantage that is tunability. Building upon the structural and functional demands outlined for highperformance EIMs, ILs emerge as a versatile class of molecular platforms ideally suited to meet these design challenges. Over the past two decades, ILs have garnered significant academic and industrial attention owing to their exceptional and tunable physicochemical characteristics.

Rather than exhaustively listing IL families, we highlight key structural motifs that underpin their application in electronic materials. Aprotic Ils, particularly 1,3-dialkylimidazolium derivatives with optimized anion pairs (Fig. 3b), dominate electrochemical applications due to their excellent ionic conductivity, low volatility, and high electrochemical stability.<sup>44</sup> These ILs often organize into nanostructured domains through

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**Fig. 3** ILs classification and structure diagram. (a) General classification of ionic liquids with an indication of a representative application area;<sup>41</sup> (b) schematic representation of the most common cations and anions described in the literature. Reproduced with permission.<sup>44</sup> Copyright 2009, Springer Nature; 2013, RSC.

a balance of coulombic, van der Waals, and hydrogen-bonding interactions, yielding microphase-separated architectures with both polar and nonpolar regions.<sup>45</sup> This feature facilitates the formation of stable, anisotropic interfaces, which is an essential requirement for emerging electronic devices and nanostructured components. In addition, ILs offer internal charge neutrality while protic ILs provide proton-conductive pathways; both types extend the functionality of ILs into soft electronics and responsive interfaces by modulating complex fluid systems (*e.g.*, nanogels, emulsions).<sup>46</sup>

By tailoring molecular constituents, ILs can be systematically designed to enhance specific performance metrics relevant to EIMs, such as interfacial stability, dielectric response, thermal robustness, or charge carrier mobility. Consequently, they serve not only as solvents or electrolytes but also as active materials capable of modulating electronic behaviour, enabling applications across fields such as energy storage, printed electronics, and sensor technologies. Therefore, the structural diversity and inherent tunability of ILs make them uniquely aligned with the design imperatives for next-generation EIMs. Their role is not ancillary but fundamental, offering a molecularlevel toolkit for achieving multi-functional integration, precision control, and high stability in device-relevant environments. The following section will delve deeper into the physicochemical properties that underpin these capabilities.

### 3 ILs-media for EIMs across dimensional scales

EIMs form the cornerstone of modern electronic and information technologies, underpinning the performance and development of integrated circuits, sensors, display technologies, communication systems, and beyond.<sup>47</sup> EIMs serve as the functional backbone of electronic hardware and are increasingly expected to meet stringent demands for miniaturization, flexibility, multifunctionality, and energy efficiency in next-generation technologies. However, as the scaling limits of silicon-based materials draw near, marked by quantum tunneling effects and thermodynamic inefficiencies at the nanoscale,48-50 conventional materials and processing techniques face diminishing returns. In this context, nanomaterials, classified by their structural dimensionality (0D, 1D, and 2D), have emerged as compelling alternatives. With unique attributes such as quantum confinement, superior charge mobility, and enhanced mechanical compliance, these materials promise to revolutionize electronics, photonics, and energy systems, enabling advances in fields ranging from wearable electronics to quantum computing.51,52

Crucially, ILs have demonstrated exceptional potential in modulating and supporting the synthesis, assembly, and performance optimization of such nanomaterials.<sup>53</sup> Their distinctive physicochemical properties, such as high ionic conductivity, tunable polarity, and strong interfacial behaviour,

offer an adaptive medium capable of guiding material growth, morphology, and interfacial interactions with atomic-scale precision. Though many IL-assisted materials have yet to achieve direct commercial deployment in electronic information technologies, their structural and functional traits align strongly with the unmet needs of the field. These include enhanced environmental stability, novel charge transport mechanisms, and tailored interface chemistry, all of which are critical to overcoming current limitations in EIMs development.

This section explores IL-facilitated advances in materials across various dimensions, ranging from 0D to 2D materials, highlighting the ways in which ILs contribute to structural control, property enhancement, and application viability within the EIMs landscape.

#### 3.1 ILs-guided engineering of 0D EIMs

0D nanomaterials, exemplified by quantum dots (QDs), have gemerged as foundational building blocks for next-generation electronic and optoelectronic devices due to their quantum size effects, tunable electronic structures, and excellent solution processability.54,55 Their size-dependent optical and electronic properties, such as bandgap tunability, high photoluminescence quantum vield, and narrow emission linewidths, have enabled significant advances in displays, photodetectors, and energyefficient lighting technologies. For instance, CdSe QDs exhibit bandgap modulation from 1.74 eV to 2.36 eV and emission tunability across the visible spectrum, with quantum yields surpassing 90%.52,55,56 While significant advances have been made with conventional synthetic approaches, exemplified by the hot-injection technique developed by Bawendi and Murray<sup>57,58</sup> (awarded the 2023 Nobel Prize in Chemistry), which enable precise control over particle size and uniformity, driving the successful integration of ODs into Samsung's OD display technology.<sup>59</sup> Despite these advantages, these methods still face limitations including reliance on costly/toxic precursors and scalability challenges.

Against this backdrop, ILs have emerged as versatile media to overcome these constraints. ILs leverage unique properties, electrostatic interactions, solvation power, and steric hindrance, that play pivotal roles in controlling particle size, dispersion, and stability.<sup>60-62</sup> Moreover, IL-mediated synthesis routes have demonstrated compatibility with green chemistry principles, minimizing the use of volatile organic solvents and enabling recyclable reaction media. These capabilities position ILs not only as enabling tools for scalable, high-quality 0D material production, but also as functional interfaces that can enhance charge transport, energy level alignment, and environmental stability when QDs are incorporated into electronic devices. Therefore, ILs serve as versatile mediators for engineering zero-dimensional information materials with atomic-level precision, offering new synthetic paradigms and interfacial functionalities critical for the advancement of EIMs.

**3.1.1 Ionic modulation in nanocrystal growth of 0D EIMs.** Building on the critical role of ILs in 0D nanomaterial engineering, their multiscale regulation mechanisms during synthesis offer a deeper insight into how atomic-level interactions translate into mesoscopic structural precision and functional enhancement. ILs provide a unique ionic environment wherein both cationic and anionic components contribute to the nucleation, growth, and stabilization of metal and semiconductor nanoparticles (NPs) through distinct but complementary mechanisms.

At the nanoscale, anions in IL are electrostatically stabilised by forming a charged protective shell around the NPs, inhibiting aggregation without the need for additional ligands (Fig. 4a).<sup>45</sup> The nature of this protective shell is consistent with the description of the EDL in Derjaguin-Landau-Verwey-Overbeek (DLVO) theory.<sup>63,64</sup> It has been demonstrated that IL ions act as discrete charged entities that counteract van der Waals attraction through space charge repulsion, thus maintaining NPs dispersion stability.<sup>65,66</sup> Au and Pd NPs are often used in optical contacts or photodetectors for nanoscale devices due to their high electrical conductivity, controlled surface catalytic activity and chemical inertness.<sup>67</sup> For example, Au NPs synthesized in  $[Bmim][BF_4]$  showed monodisperse size distributions, significantly outperforming other ILs, which vielded larger particles under otherwise comparable conditions.65 In addition, the type and functionality of the IL anion markedly influence not only particle size but also oxidation resistance and formation kinetics. Hydroxylfunctionalized ILs, such as [C2OHmim]-based systems paired with [OTf], [TFA], or [Tf<sub>2</sub>N] anions, have been shown to produce Pd NPs with smaller average diameters (2.3-4.0 nm) and greater oxidation resistance compared to their non-functionalized analogues.68

On a molecular level, ILs form spatially resolved interfacial structures around growing nanocrystals. Electrostatic stabilization is often mediated by layered arrangements, initial anion adsorption followed by loosely ordered cationic shells (Fig. 4b). The thickness of these EDL (typically 2.8-4.0 nm) depends on anion size and symmetry.<sup>69,70</sup> For instance, the oblique adsorption of asymmetric [Tf<sub>2</sub>N] anions on positively charged surfaces creates a dynamic cis-oriented solvation interface, enhancing colloidal dispersion and impeding sintering.<sup>71</sup> The Ir nanoparticle-based TTA conversion system is capable of continuous modulation of the emission spectrum from orange (580 nm) to blue (460 nm).<sup>72</sup> Upon synthesis of Ir (0) NPs in ILs, SAXS and XPS analyses confirmed the formation of conformal IL layers with precise spatial dimensions (~2-4 nm), which remained associated with the particle surfaces even after isolation.73

Cations of ionic liquids can also coordinate with the surfaces of metal NPs (Fig. 4b). For example, in the case of the interaction between [Bmim] cations and Ag NPs, the cation coordinates with the particle surface in a flat configuration, forming a positively charged protective layer, while  $[BF_4]$  anions do not chemically interact with the particle surface (Fig. 4b).<sup>79</sup> Additionally, the electrostatic layer formed by the interaction of [Emim] cations with the surface of silica has a thickness of 0.5 nm, while the thickness of the



Fig. 4 ILs-guided 0D material construction: (a) anion-based electrostatic stabilization;<sup>45</sup> (b) cation coordination;<sup>74</sup> (c) ion-pair stabilization;<sup>75,76</sup> (d) micelle formation.<sup>45,77,78</sup> Copyright 2008, ACS; 2014, RSC and 2016, Elsevier.

second solvation layer is 1.15 nm, indicating subtle interactions between the cation and the surface.<sup>74</sup> Furthermore, in ILs systems, cations and anions act cooperatively as structured ion pairs to form well-ordered interfacial monolayers (Fig. 4c).<sup>80</sup> This behaviour has been reported at Pt and Ru surfaces, where ion pair orientation depends on surface charge and contributes to enhanced nanoparticle stability (Fig. 4c).<sup>75,76</sup> Classical DLVO models suggest that the high ionic strength and spatial heterogeneity of ILs favor such ordered interfacial architectures, balancing electrostatic repulsion with van der Waals attractions to achieve thermodynamically stable dispersions.<sup>63,64</sup>

Taken together, these findings highlight that ILs act not merely as passive media but as active regulators of nanocrystal formation and surface structure through multiscale ionic interactions. Their ability to orchestrate electrostatic, coordinative, and steric stabilization mechanisms positions them as powerful tools in the rational design of 0D EIMs with enhanced precision, stability, and device integration potential.

**3.1.2 ILs-driven green nanofabrication of 0D EIMs.** In the pursuit of environmentally benign and structurally precise 0D EIMs, ILs offer not only chemical tunability and low volatility but also unique self-assembly behaviors that enable green synthesis strategies. Beyond their intrinsic ionic interactions discussed in section 3.1.1, ILs can participate actively in micro-structured environments, such as micelles and microemulsions, serving as templating agents, phase stabilizers, and growth modulators in the fabrication of 0D nanomaterials.<sup>45,77</sup>

ILs combined with conventional surfactants can form micellar structures, effectively controlling the size and morphology of nanoparticles (Fig. 4d). The ability of micellar aggregates formed by polymeric ILs to control the size of gold nanoparticles, as well as the effect of IL concentration, was proposed by Li.<sup>77</sup> At low metal salt concentrations, vesicular assemblies form with uniformly distributed 4 nm gold NPs localized at the bilayer interfaces (Fig. 4d). In contrast, higher precursor concentrations favor the formation of dense, spherical micelles yielding larger NPs (~10 nm), emphasizing the role of electrostatic repulsion between IL cations in suppressing aggregation within confined environments. This micellar templating effect extends to other systems as well. In aqueous IL-surfactant solutions, e.g., dodecyltrimethylammonium bromide, a-FeOOH NPs exhibited smaller sizes and higher dispersion uniformity compared to control samples lacking ILs. It was proposed that IL headgroups associate with hydroxylated iron oxide surfaces while the hydrophobic tails extend outward, forming reverse-micelle-like structures that encapsulate the growing particles (Fig. 4d).<sup>78</sup> Additionally, the nature of the solvent modulates micellar structuring and nanoparticle formation.

A more versatile and scalable approach involves IL-based microemulsions, which allow the dispersion of otherwise immiscible phases and enable control over nanostructure dimensions, while also addressing challenges such as precursor solubility and high IL viscosity.<sup>81</sup> In these ternary or quaternary systems, ILs can simultaneously serve as the polar phase, nonpolar medium, and even as surfactant components, creating a unified platform for soft templating.<sup>82,83</sup> This approach not only eliminates volatile organic solvents but also enhances system conductivity and thermal stability, making it particularly suitable for the fabrication of high-purity 0D materials for electronic applications. In addition, the structural control within ILbased microemulsions arises from the nanodroplet templating effect. Higher IL surfactant concentrations result in smaller and more numerous NPs, while an increase in the

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water phase under fixed IL/surfactant ratios leads to larger particle sizes, in line with droplet swelling phenomena.<sup>83,84</sup>

These studies underscore the emerging paradigm wherein ILs function not only as reaction media but as active supramolecular directors in green synthesis. Through micellar self-assembly and nanodroplet confinement, ILs allow environmentally friendly and compositionally versatile control over 0D nanomaterials, paving the way toward scalable, sustainable, and morphologically tunable platforms for next-generation electronic information technologies.

#### 3.2 ILs in 1D EIMs: harnessing quantum effects

1D nanomaterials are regarded as a robust substitute for silicon-based materials in the domains of nanoelectronics and quantum devices. This is due to the quantum-limited domain effect in the transverse dimension and the intrinsically high carrier mobility, which exhibits excellent electron transport properties and size tunability.1D materials generally refer to nanostructures with high aspect ratios, such as nanowires, nanotubes, and nanorods.

**3.2.1 Quantum confinement effects and fabrication challenges.** Quantum confinement effects dominate the

electronic behaviour of 1D EIMs when their characteristic dimensions enter the sub-10 nm domain. This reconfigures the carrier transport mechanism through energy level discretisation. Theoretical studies show that this effect suppresses electron-phonon scattering (increasing the probability of ballistic transport to 85%) and modulates the Fermi energy level depending on its size. This provides a physical basis for 1D materials outperforming conventional silicon-based devices (Fig. 5a).85,86 Research shows that specific chiral CNTs with a diameter of 2 nm have a mobility exceeding  $10^5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  and a saturation velocity of  $4 \times 10^7$ cm s<sup>-1</sup> at room temperature. This is two orders of magnitude and four times higher, respectively, than silicon materials.<sup>87</sup> In contrast, Cu nanowires with a surface step height of less than 0 nm have a lower mobility 5 nm were successfully fabricated through morphological engineering to achieve maximum absorption close to 100 per cent (99.98 per cent) and form ohmic contacts in the deep ultraviolet region.88,89

Despite significant progress being made, the preparation for scaling up and interfacial modulation remain key bottlenecks. In contrast to chemical vapour deposition (CVD), which can produce high-quality CNTs ( $I_D/I_G < 0.05$ ) but is costly and limited in practicality, solution stripping can



Fig. 5 Representative roles of ILs in 1D EIMs. (a) CNT-based air-channel device;<sup>85</sup> (b) IL-induced growth of ZnO nanorods;<sup>93</sup> (c) IL-guided assembly of ZnS nanowires on gold templates;<sup>99</sup> (d) IL-assisted synthesis of CNT/Fe–N–C electrocatalysts for ORR.<sup>101</sup> Copyright 2023, ACS and 2011, 2021, RSC.

control the diameter deviation within 5% at a tenfold cost reduction by optimizing the solvent system (e.g., DMF/water = 3:1).<sup>90,91</sup> At the device level, contact resistance can account for up to 70% of the total resistance, which makes it a significant obstacle to improving performance. However, recent interface engineering breakthroughs demonstrate that self-assembled monolayer (SAM) modification can reduce the Schottky barrier by 40% ( $\Delta \Phi = 0.12$  eV), while gradient metal stacking (Ag/TiN/Pt) can depress the contact resistance to  $8 \times$  $10^{-8}$   $\Omega$  cm<sup>2</sup>.<sup>92</sup> These advances reveal that industrial translation of the quantum advantages of 1D materials requires the synergistic optimisation of bottom-up synthetic control and top-down interface design. As discussed in section 2, interfacial modification techniques using ILs provide an innovative solution to the paradox of contact resistance and thermal stability, and are expected to bridge the gap between the properties of quantum confinement and fabricatable device architectures.

3.2.2 ILs as enablers for 1D EIMs' morphological control and functionalization. The unique role of ILs as "intelligent soft templates", as described in the previous section, also demonstrates excellent capabilities in the precise synthesis, assembly and functionalisation of 1D materials (Fig. 5b).93 1D carbon nanomaterials occupy a key position in the construction of flexible energy and nanodevices, and ILs intelligent modulation has shown direct results in the modulation of their dispersion and optimisation of their interfacial electronic behaviour. Li prepared metal-free catalysts by introducing imidazolium-based ILs into CNTs through an in situ functionalization strategy, which significantly enhanced their performance in electrocatalytic hydrogenolysis reaction (HER).94 ILs has also been used as a dispersant in polymer complexes. ILs enable CNTs to form a continuous conductive network in PLA/EVA matrix, which significantly enhances the dielectric and mechanical properties of the composites.95 CNTs functionalized based on ILs have also been used to construct highly sensitive electrochemical sensors exhibiting good response properties.<sup>96</sup>

1D semiconductor nanowires, including ZnS and Sb nanowires, are of significant importance as fundamental components in the fabrication of high-density electronic devices and micro/nano-sensing platforms.<sup>97,98</sup> In related studies, a variety of nanowire systems with fine structures and outstanding functions have been successfully constructed using different ionic liquid environments. ZnS nanowires with diameters of less than 50 nm and lengths of up to 10  $\mu$ m and centimetre-sized ZnS single-crystal nanowires with aspect ratios of more than 10<sup>5</sup> have been synthesised in the presence of [Bmim][BF<sub>4</sub>] (Fig. 5c).<sup>99</sup> Si nanowires with low deviation etching were realised using [Py1,4][TfO].<sup>100</sup> Furthermore, Si/Tb nanowire structures with homogeneous axial components and room-temperature visible luminescence with millisecond lifetimes were prepared under the template-assisted method (Fig. 5d).<sup>101</sup>

Boron nitride nanotubes (BNNTs) have been limited in structure functionalisation due to their broad forbidden band and chemical inertness.<sup>102</sup> The introduction of IL provides a novel concept for surface modification.<sup>103-105</sup>

Hossein investigated the effect of modifications to different organic functional groups (*e.g.*  $CH_3CO$ , 2-methoxy-*N*,*N*dimethylethylamine) on the electronic structure of BNNTs. This investigation was based on density functional theory (DFT). The study found that ionic liquid functionalization can significantly enhance the electrical conductivity and chemical softness of BNNTs. This lays the foundation for the practical application of BNNTs in aqueous and nonaqueous media.<sup>106</sup>

In summary, IL-assisted 1D material synthesis and functionalization strategy not only promotes the efficient construction of a variety of typical quantum-limited domain structures, but also significantly improves the interfacial properties and integrability of device-level materials. This structural foundation and interfacial guarantee is essential for the large-scale application of 1D EIMs.

#### 3.3 ILs-mediated engineering of 2D EIMs

In the context of EIMs, the dimensionality of the material in question exerts a direct influence on its physicochemical properties and the potential applications thereof. In comparison to 0D EIMs, where carrier localisation is severe and efficient transport is challenging to achieve, and 1D EIMs, where electrical conductivity is limited, 2D EIMs achieve a high degree of synergy between electronic and structural properties. This is due to their atomically hierarchically ordered structure, high carrier mobility and excellent mechanical compliance.<sup>114,115</sup> Typical 2D EIMs, such as graphene, transition metal dihalides (TMDs) and black phosphorus (BP), are rapidly becoming key material platforms for next-generation nanoelectronic and optoelectronic devices due to their atomic-level thickness, dangling-bond-free surface structure and excellent compatibility with van der Waals heterostructures in FETs (Fig. 6a).<sup>107</sup>

Similarly, ILs have demonstrated significant potential in the study of 2D EIMs. Their multifaceted functions, ranging from exfoliation solvents and stabilizing agents to reaction accelerants and structural modulators, enable precise manipulation of 2D nanosheet morphology, thickness, and electronic properties. This section focuses on the primary application directions of ILs in 2D materials.

**3.3.1 ILs in liquid-phase exfoliation of traditional EIMs.** Graphene, the most representative 2D material, has attracted significant attention from the research community in the field of developing next-generation electronic devices (*e.g.* high-frequency transistors, photodetectors) due to its fascinating electrical and optical properties.<sup>116,117</sup> In order to achieve the potential of the aforementioned device applications, it is imperative that a breakthrough in efficient macro-preparation is realised. The fabrication of graphene can be achieved through a variety of methods, including exfoliation, CVD, and reduction of graphene oxide.<sup>118,119</sup> CVD is regarded as one of the most promising techniques for the industrial production of graphene (Fig. 6b).<sup>91</sup> It is unfortunate that the preparation of materials by this method frequently necessitates the use of costly catalysts.<sup>120</sup> However, graphene films grown on solid substrates in the CVD process are

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**Fig. 6** IL-mediated for 2D EIMs. (a) Morphology and spectral features of vertical field-effect transistors (FETs) based on 2D EIMs), along with a schematic of their integration in sliding-mode triboelectric nanogenerators (TENGs);<sup>107</sup> (b) scalable graphene production methods;<sup>91</sup> (c) microwave-assisted synthesis;<sup>108,109</sup> radical-induced exfoliation intercalation;<sup>110</sup> (d) TRPIL-assisted exfoliation of layered materials;<sup>111</sup> (e) schematic diagram exfoliation of bulk BP;<sup>112</sup> (f) structure and stacking of h-BN nanosheets.<sup>113</sup> Copyright 2024 WILEY; 2018 MDPI; 2015 RSC and soon.

difficult to transfer to other substrates for further applications.<sup>121</sup> Liquid phase exfoliation (LPE) is widely regarded as the most promising technology for industrialisation due to its ambient temperature and pressure operation, adjustable solvents, simple equipment and continuous production advantages.<sup>122,123</sup> The core mechanism of IL-assisted stripping, as an optimised branch of LPE, relies on strong cation– $\pi$  interactions between IL cations and graphite layers, significantly improving stripping efficiency and overcoming the limitations of conventional organic solvents.<sup>124</sup>

This technique enabled the preparation of graphene nanosheets (GNs) with concentrations reaching up to 5.33 mg

 $\rm mL^{-1.125}$  Subsequent STEM/XPS characterisation confirmed that the products exhibited ultrathin structures (*i.e.* comprising fewer than five layers), low defect rates and high crystalline integrity.<sup>126–128</sup> These properties are essential for preserving the intrinsic electrical properties of graphene and for constructing high-performance heterojunction devices.<sup>109</sup> The continuous advancement of IL in the field of material optimisation is driven by the utilisation of microwave assistance. The process of microwave assistance involves subjecting graphene oxide (GO) to a treatment at 200 °C for a duration of 40 minutes, resulting in the acquisition of high-conductive, reduced graphene oxide (RGO) with an enhanced electrical conductivity of 4 times. RGO

demonstrates remarkable performance as an electrical capacitor, exhibiting a capacitance of 135 F g<sup>-1</sup> at 3.5 V (Fig. 6c).<sup>108</sup> The chemical dissolution method employs [C<sub>8</sub>mim][PF<sub>6</sub>] or watersoluble IL (*e.g.*, [Bmim][BF<sub>4</sub>]) in the [C<sub>8</sub>mim][BF<sub>4</sub>] system for the preparation of films with a thickness of up to 1 nm. As illustrated in Fig. 6c, the 1 nm thick sensory fossil layer exhibits both efficiency and adaptability in terms of its manufacturing process.<sup>110,129</sup>

In addition to playing a key role in LPE of graphene, ILs also show unique advantages in the transfer of monolayer graphene. The utilisation of poly(ionic liquid) (PIL) 1-vinyl-3ethylimidazolium bromide in the formation of [PIL][Br]-G complexes with GO has resulted in the development of a water-soluble system. This system facilitates the reversible phase transfer of reduced RGO between aqueous and organic solvents. Subsequent addition of lithium salt ([Li][Tf<sub>2</sub>N]) to this system induced an anion exchange between [Br] and  $[Tf_2N]^-$  to form  $[PIL][NTf_2]$ -G complexes that are soluble in organic phases, thus further expanding the application of graphene in the field of electronic information technology (Fig. 6c). In the presence of [C<sub>12</sub>mim][Br], GO dispersed in the aqueous phase can be transferred to non-polar organic solvents such as *n*-dichlorobenzene. Following hightemperature annealing, the sp<sup>2</sup> properties of RGO are restored, resulting in electrical conductivity levels of up to 823 S cm<sup>-1</sup>.<sup>130</sup>

**3.3.2 ILs in exfoliation and functionalization of emerging 2D EIMs.** The maturation of LPE has led to its application being extended from graphene to a wider range of novel 2D EIMs. These include TMDs, BP and BNNTS. It is evident that each of these materials exhibits distinct electronic structural advantages. However, their interlayer bonding strength, surface activity and chemical stability differ significantly, thereby necessitating disparate requirements with regard to the exfoliation mechanism and interface regulation strategy. ILs as an interfacial medium with a highly designable molecular structure, demonstrates unique advantages in regulating the dispersion of the lamellae, the electronic integrity and the environmental adaptability.

MoS<sub>2</sub>, typical materials of TMDs, exhibits excellent flexibility and tunability, making it highly promising for applications in energy storage devices and flexible displays.<sup>131</sup> A simple one-pot sonication approach yielded MoS<sub>2</sub> sheets with intact crystallinity and smooth layered structures, achieving a monolayer yield exceeding 50%.<sup>132</sup> Further systematic analysis revealed that the exfoliation efficiency of the [Bpy][X] series of ILs ( $X = [BF_4]^-, [PF_6]^$ and  $[Tf_2N]^-$  is closely related to their intermolecular aggregation capabilities. The results indicated that among the nine studied IL compounds, the [Bpy][X] combinations  $(X = [BF_4]^{-}, [PF_6]^{-}$  and  $[Tf_2N]^{-}$ ) exhibited the strongest aggregation abilities. This finding suggests that intermolecular bonding within the [Bpy][X] systems plays a critical role in enhancing the intercalation-exfoliation efficiency of the solvents.<sup>133</sup> By optimising the growth and exfoliation interfaces, Gao et al. found that bulky cations (e.g. imidazolium) in IL can adsorb synergistically with the MoS<sub>2</sub> surface via  $\pi$ -d interactions, significantly enhancing the interlayer

lubricity and intercalation efficiency, leading to the acquisition of high-quality monolayers of  $MoS_2$  with preservation of the inplane lattice ordering and photoresponsive properties.<sup>134</sup>

Furthermore, thermostable PIL (TRPIL) provides a dynamic peeling strategy (Fig. 6d). At low temperatures, hydrophobic interactions drive peeling through  $\pi$ - $\pi$  stacking, while at high temperatures, steric hindrance from hydrophilic structural domain expansion inhibits reaggregation. In this manner, dual-responsive TRPIL/MoS<sub>2</sub> composites for smart hydrogels and high-strength pearl-like films were developed.<sup>135</sup>

BP has found widespread application in near-infrared (NIR) optoelectronic devices, a testament to its tunable bandgap and high mobility.<sup>136,137</sup> The achievement of high stability liquidphase stripping of BP is a key prerequisite for its application in the fabrication of optoelectronic devices. China Electronics Technology Group Corporation's patent for a BP-based infrared detector and a prototype BP field effect transistor device developed by STMicroelectronics highlight the importance of BP in this field.<sup>138</sup> However, its strong oxygen sensitivity severely limits its liquid phase processing window. Zhao prepared highly concentrated, air-stable monolayer to few-layer BP dispersions using ILs such as [Hoemim] [TfO].139 The monolayers obtained from the dispersion of BP nanosheets in ambient air demonstrated stability for up to one month, exhibiting excellent stability. In a similar manner, Lee et al. demonstrated that [Emim] [Tf<sub>2</sub>N] and [Bmim] [Tf<sub>2</sub>N] not only efficiently removed BP by ultrasonication, but also protected the BP from oxidative degradation by the IL-derived passivation layer. This resulted in scalable processing under ambient conditions. The multilayered BP dispersions obtained have unexpectedly high antioxidant activity as well as chemical and structural integrity (Fig. 6e).<sup>112</sup> Known as "white graphene", BNNS offer excellent thermal conductivity and dielectric performance (Fig. 6f), showing great potential for applications in thermal management, highfrequency electronic devices, and flexible packaging.<sup>113</sup> However, their large-scale exfoliation has been limited. ILs with surface energies comparable to h-BN, such as [Bmim] [PF<sub>6</sub>] and [Bmim]  $[Tf_2N]$ , facilitate effective exfoliation through cation- $\pi$  and hydrogen bonding interactions.<sup>140–142</sup> Systematic studies suggest that the anion plays a more decisive role than the cation in determining exfoliation efficiency and final concentration, with the general trend:  $[PF_6] > [Tf_2N] > [BF_4] > [TfO]$ , reflecting differences in anion basicity and hydrogen bonding ability.<sup>141</sup>

In summary, ILs exhibit remarkable versatility and tunability in the synthesis, functionalization, and performance optimization of EIMs spanning 0D, 1D, and 2D systems. For 0D materials such as QDs, ILs enable precise control over particle size, shape, and surface chemistry, thereby enhancing their optical and electronic properties. In 1D systems including CNTs, metal nanowires, and semiconductor nanowires, ILs facilitate selective dispersion, alignment, and doping, contributing to improved electrical conductivity and mechanical integrity. Most notably, in the context of 2D materials, ILs serve as green and highly designable media for efficient LPE and stable dispersion of graphene, TMDs (e.g., MoS<sub>2</sub>), BP, and BNNTs. Through noncovalent interactions, thermoresponsive behaviour, and tailored ion-surface

interactions, ILs not only enhance exfoliation yield and material stability but also unlock new routes for multifunctional device integration. These insights collectively underscore the immense potential of ILs as multifunctional agents in the development of next-generation EIMs and devices, offering a powerful platform for green, scalable, and high-performance material engineering across all dimensional hierarchies.

# 4 ILs in high-purity separation and purification of ECs

In the synthesis of ECs and device fabrication, impurity control and high-purity separation of products are key technical steps to ensure material performance and device stability.54,143 In synthesis, purification and process, a variety of metal ion impurities are often introduced or residual, and the main sources of these metal ions include catalyst residues, raw material impurities, equipment corrosion products and process pollution. Among them, platinum group metals (Pt(v), Pd(u), Rh(u)) and heavy metal ions (e.g.,  $Cr^{3+}$ ,  $Ni^{2+}$ ,  $Cu^{2+}$ ,  $Zn^{2+}$ ,  $Cd^{2+}$ ) are most representative. The presence of impurities such as metal ions, organic by-products, isomers and solvent residues can trigger electrical property fluctuations and interfacial defects, directly affecting device reliability.144,145 Given the demands for high integration, complex process systems, and ultra-trace impurity control, traditional techniques such as distillation, crystallization, extraction, and membrane separation still have limitations in terms of selectivity, energy consumption, and environmental sustainability.146 Owing to their exceptional molecular designability, tunable polarity, and diverse solvation mechanisms (ion exchange, hydrogen bonding,  $\pi$ - $\pi$  interaction, hydrophobic association, etc.), ILs have emerged as versatile tools for selective and efficient separation in electronic chemical production.<sup>147,148</sup> This section outlines recent advances in IL-enabled separations, focusing on two major categories: (1) metal ions and organic intermediates, and (2) hydrocarbon feedstocks and complex impurities. The corresponding applications, separation mechanisms, and design strategies are discussed, along with industrial demonstrations and emerging trends.

## 4.1 ILs for metal ion extraction and organic intermediate separation

With regard to the separation of metal ions, ILs have been demonstrated to selectively capture target ions by means of a number of mechanisms, including but not limited to chelation, ion exchange and hydrogen bond complexation. For metal ion extraction, ILs enable high-efficiency separation *via* chelation, ion exchange, and specific solute–IL interactions. For example, imidazolium-based ILs achieve over 90% extraction efficiency for platinum-group metals (Pt(rv), Pd(II), Rh(III)) at elevated temperatures with rapid equilibrium kinetics (Fig. 7a).<sup>149</sup> Cao studied the performance of 1-butyl-3-methylimidazolium hydrogen sulfate ([Bmim][HSO<sub>4</sub>]) and sulfonated functionalized imidazolium salts ([PrSO<sub>3</sub>Hmim][HSO<sub>4</sub>]) in the removal of heavy metals from electroplating sludge. The results showed that the

latter achieved removal efficiencies of 99.8%, 90.1%, and 91.3% for Cr, Ni, and Cu, respectively, significantly higher than non-functionalized ILs (Fig. 7b). $^{150}$ 

The incorporation of chelating functional groups into ILs structures significantly enhances their affinity for metal ions, thereby enabling highly selective and efficient extraction. This design strategy has led to the development of task-specific ILs that can be immobilized within solid matrices, such as polymeric resins, creating hybrid systems that combine the molecular tunability of ILs with the operational ease and recyclability of solid sorbents. Such IL-impregnated resins have shown remarkable performance in the selective recovery of metal ions like Zn<sup>2+</sup> from complex aqueous environments, underscoring the growing potential of IL-based composite materials in advanced Moreover, ammoniumseparation technologies.<sup>154</sup> and phosphonium-based ILs functionalized with tailor-made anions have exhibited strong extraction capabilities for a range of heavy metals, including cadmium, copper, and zinc, demonstrating the versatility of IL chemistry in addressing diverse separation challenges.<sup>155</sup> Importantly, the efficiency of these systems is influenced not only by the chemical nature of the IL but also by operational factors such as contact time, suggesting opportunities for process optimization. These findings collectively affirm the strategic advantage of ILs in the design of next-generation, highperformance separation platforms for critical metal recovery.<sup>156</sup>

In the synthesis pathway of bioelectrochemicals, smallmolecule organic acids such as lactic, succinic, acetic and nicotinic acids are widely used as functional precursors for the preparation of electronic-grade materials (e.g., polymer dielectrics, photoresist precursors or functional electrode additives). Consequently, the meticulous extraction of these precursors from reaction residues or fermentation broths is of significant value in enhancing yield and purity.<sup>152</sup> Taking nicotinic acid as an example, [C<sub>6</sub>mim][ClO<sub>4</sub>] exhibits excellent separation performance during its extraction, where the main driving forces include hydrogen bond donation from the IL cation to the carboxyl group of nicotinic acid, along with synergistic effects of  $\pi$ - $\pi$  stacking and hydrophobic interactions.157 Fan achieved a recovery rate of 91.7% for nicotinic acid using 0.1 mol L<sup>-1</sup> HCl desorption, and further demonstrated the multiple recycling capability of the IL system after drying at 70 °C for 4 h. In the naphthenic acid system, Geng et al. employed imidazolium carbonate-based ILs ([Emim]<sub>2</sub>CO<sub>3</sub>, [Emim]NO<sub>3</sub>, [Emim]HSO<sub>4</sub>) to achieve efficient extraction under conditions of 40 °C, an IL-to-oil mass ratio of 0.010, a stirring speed of 500 rpm, and a contact time of 1 h, with efficient IL regeneration accomplished via hydrochloric acid reflux (Fig. 7c).<sup>151</sup>

Further studies on process integration indicated that ILs combined with liquid membrane separations, such as spiral module supported liquid membranes (SLM) and emulsion liquid membranes (ELM), exhibit outstanding performance in the separation of lactic acid and succinic acid, as illustrated in the schematic diagram in Fig. 7d. Marták *et al.* utilized a Cyphos IL-104 loaded liquid membrane system supported by PTFE, achieving a high mass transfer coefficient and stable membrane



Fig. 7 IL-mediated separation mechanisms: (a) esp map and extraction of Au(III), Pd(II), Pt(IV);<sup>149</sup> (b) removal of Cr, Ni, and Cu;<sup>150</sup> (c) [Emim]-based extraction mechanism;<sup>151</sup> (d) IL-SLM separation;<sup>152</sup> (e) reverse micelle-driven transport process.<sup>153</sup> Copyright 2022, MDPI and 2008, 2021, 2022, ELSEVIER.

operation for 5.3 days during lactic acid recovery.<sup>158,159</sup> The ILEM system developed by Khan *et al.*, using [Tmam][Ac] as both emulsifier and carrier, achieved a lactic acid separation efficiency of 94.5%, further confirming the process compatibility of ILs in liquid membrane systems (Fig. 7e).<sup>153</sup> In the recovery of carboxylic acids and bio-fermentation products, ILs achieve high-

selectivity and high-purity extraction through synergistic mechanisms including hydrogen bond complexation, hydrophobic association, and reverse micelle formation. The integration of liquid membrane technology is expected to further enhance the mass transfer efficiency and process sustainability of IL-based separation systems.

## 4.2 ILs for hydrocarbon separation and complex impurity removal

In the manufacture of high-end electronic chemicals (e.g. electronic-grade solvents, dielectric monomers, photoresist materials, etc.), light hydrocarbon compounds are frequently incorporated into the system as synthetic precursors, diluents, or reaction by-products. Furthermore, some of the hydrocarbons are derived from petrochemical feedstock deep-processing or residues from polymerisation reactions. Typical hydrocarbon impurities include C1-C4 grade straight chain paraffins (e.g. methane, ethane, propane), unsaturated hydrocarbons (e.g. ethylene, propylene, butyne), isomeric alkanes (e.g. isobutane), and alkylation by-products. While these small-molecule hydrocarbons possess inherent value in the pre-fabrication stage of electronic materials, effective separation during subsequent product refinement is imperative to avoid significant interference with the purity regulation of key components, the induction of undesirable side reactions, or degradation of device performance.<sup>160</sup> Conventional cryogenic distillation and extractive distillation are limited in their application to green separation technologies due to their high energy consumption and issues related to organic solvent volatilization. ILs, by virtue of their  $\pi$ -electron-rich cations and tunable anions, can selectively solubilize unsaturated hydrocarbons via  $\pi$ - $\pi$  and van der Waals interactions.161,162 In olefin/paraffin separation studies, numerous works have demonstrated that imidazoliumbased ILs can effectively enhance ethylene solubility in ethylene/ ethane systems, and that separation performance can be further optimized by tuning the cation side-chain length and anion charge density.<sup>163</sup> Beyond hydrocarbons, ILs are also effective in removing phenolic compounds, dves, herbicides, and complex metal-organic contaminants from electronic-grade solvents.<sup>164</sup> By designing ILs with specific functional groups, selective extraction of complex pollutants can be achieved, and coupling with technologies such as membrane separation and adsorption can enhance the overall process's flexibility and environmental friendliness.165

As discussed above, ILs offer a transformative platform for the separation and purification of ECs, addressing key challenges associated with impurity control, molecular selectivity, and process sustainability.166 Their unique physicochemical properties, including tunable polarity, strong solvation capabilities, and diverse interaction mechanisms such as hydrogen bonding,  $\pi$ - $\pi$ stacking, ion exchange, and hydrophobic association, enable highly efficient and selective extraction of metal ions, organic acids, and hydrocarbon species. Moreover, the integration of ILs into advanced systems, such as task-specific resins and liquid membranes, further enhances their applicability in complex separation scenarios. These advances not only improve the purity and stability of electronic-grade materials but also align with the growing demand for green and energy-efficient processes. As research continues to optimize IL structures and recovery strategies, IL-based separation technologies are poised to play a critical role in the development of next-generation EIMs and sustainable chemical manufacturing.

### 5 ILs-enabled electronic devices

Building upon the previous discussions on the regulatory mechanisms of ILs in semiconductor nanomaterials, this section will focus on the value of ILs in electronic devices, particularly their applications in addressing key challenges in the interface engineering of high-performance electronic devices.

#### 5.1 Electric double layer modulation in field-effect transistors

FETs, as the core components in electronic devices, function based on the core mechanism of gate voltage control over carrier distribution, modulating the semiconductor channel's band structure and carrier concentration through the gate electric field, thereby dynamically controlling the formation and cutoff of conductive channels to achieve low-power, high-sensitivity current-switching functionality (Fig. 8a).<sup>22</sup> This physical process is primarily achieved through the formation of the EDL at the electrolyte-electrode interface.<sup>167</sup> Effective gate control of the FETs requires meeting four key criteria: (1) the distance between the gate and the molecules should be minimized to ensure that the electric field can directly and effectively act; (2) achieving high electrostatic coupling strength, which can be quantified by the  $\xi$ parameter;<sup>18</sup> (3) the dielectric layer must have a high dielectric constant  $(\varepsilon_r)$  to enhance charge accumulation capability;<sup>168</sup> and (4) suppressing the shielding effect of the source-drain electrodes on the gate electric field.<sup>168-170</sup>

ILs, due to their exceptionally high field-effect coupling capabilities, are particularly well-suited for the ideal gate modulation described above. When a gate voltage is applied, compared to traditional electric double layer interfaces, the cations and anions in ionic liquids can form an ultrathin EDL at the electrode-semiconductor interface under very low voltages.<sup>174</sup> The EDL formed by ILs at the electrode-semiconductor interface can induce carrier concentrations on the order of  $10^{14}$ – $10^{15}$  cm<sup>-2</sup>. Compared to traditional solid-state dielectric layers, the EDL of ILs allows for effective modulation at low gate voltages (<2 V), significantly reducing switching power consumption.<sup>175–178</sup>

The thickness of the EDL in ILs can be tuned to the subnanometer scale through ion size. For example, [Bmpy][FAP], the EDL thickness is only 8 Å, significantly lower than the traditional solid-state gate (about 5 nm), thus generating a higher electric field strength under the same voltage.<sup>179</sup> The conductivity of the meta-benzenethiol (meta-BT) molecular junction, gated by [Bmim][PF6], decreases by two orders of magnitude at a -0.4 V gate voltage compared to 0 V (Fig. 8b), confirming the precise tuning capability of ILs over destructive quantum interference (DQI) effects.<sup>25</sup> Similarly, the 2,4-TP-SAc molecule achieves a ~100-fold on/off ratio within the range of -0.6 V to -0.4 V (vs. Ag/AgCl) and -0.4 V to 1.4 V (Fig. 8c), verifying the feasibility of continuous IL modulation of the DQI effect to construct high-performance monomolecular devices.<sup>26</sup> Additionally, a vertical molecular tunneling field-effect device constructed using pseudo-para-





diphenylacetylene-*p*-(2,2)-cyclohexane (PCP) achieved a  $\sim$ 330 on/off current ratio based on an ILG.<sup>180</sup> The vertical molecular tunneling field-effect devices (such as the PCP structure) achieved a  $\sim$ 330 on/off ratio through ILG, further extending the application boundaries of ILs in nanoscale electric field modulation.<sup>180,181</sup>

In addition, ILs high dielectric constant property greatly improves the efficiency of the interfacial charge response. This is evident in various experimental systems. In dynamic junctions (*e.g.* platinum to electrode systems), the EDL formed after applying a voltage can effectively control carrier transport in single-molecule junctions. In static junctions (*e.g.* graphene dot electrode systems), the gate-induced EDL can finely regulate the alignment of molecular orbitals with the electrodes Fermi energy levels. In particular, in fourelectrode dynamic junction systems with an Ag/AgCl reference electrode, the high-dielectric-constant IL enables the potential applied to the working electrode to modulate its energy levels almost exclusively, achieving extremely high modulation efficiency and significantly reducing the effects of electrode polarisation and solution IR pressure drop (Fig. 8d).<sup>171</sup>

Recent advances in research, particularly in the field of iongated transistors (IGTs) and their derivatives (*e.g.* emerging iongated vertical transistors (IGVTs)), have highlighted the great potential of ILG in optimising the performance of a wide range of low-dimensional semiconductor devices. IGVTs can achieve the long- and short-term enhancement properties required for neuromorphic computation at brain-like processing rates and low power consumption, as well as optimising plasticity by enabling the programmable tuning of the doping mechanism (electrochemical/electrostatic) and time resolved properties through the precise control of gating parameters (Fig. 8e).<sup>172</sup> Notably, the IGVTs architecture demonstrates faster data processing speeds and higher storage densities than conventional devices under low-voltage and low-power operation. It also successfully realises multimodal (vision, touch, taste and hearing) bionic sensory integration, providing a powerful technological route for developing high-performance, multifunctional neuromorphic systems (Fig. 8f).<sup>173</sup>

#### 5.2 ILs for flexible and transparent wearable electronics

Wearable electronic devices are emerging as foundational components of next-generation electronic information systems due to their inherent flexibility, environmental adaptability, and portability.<sup>182,183</sup> However, they pose demanding material requirements, including optical transparency, mechanical flexibility, and scalable processability, criteria often unmet by conventional substrates.<sup>184</sup> For instance, polyimide (PI), though thermally robust and mechanically strong, suffers from poor visible light transmittance due to its intrinsic chromophores structure. Attempts to improve transparency through chemical modification or nanoparticle doping often compromise flexibility or introduce processing complexity.<sup>185-188</sup>

ILs offer a transformative solution. When integrated into PI systems, ILs, especially those bearing trifluoromethyl or large anions like [TFSI]-, simultaneously enhance optical transparency, flexibility, and thermal conductivity.<sup>189</sup> ILmodified Kapton film shows an increase in transmittance from 76% to 84.8% at 550 nm, while IL-modified Kapton film shows an increase in transmittance from 76% to 84.8% at 550 nm, while cutoff wavelength ( $\lambda_{cutoff}$ ) decreases from 411 nm to 373 nm.<sup>184</sup> Furthermore, ILs combine with the PI side chains through hydrogen bonding, significantly improving the material's flexibility. The L1/CPI sample with 8 wt% ILs achieves a fracture elongation of 108.4% (pure CPI is only 2.9%), and the tensile modulus decreases from 2929.6 MPa to 844.6 MPa, enabling the transition from brittleness to toughness.<sup>190,191</sup> The molecular structure of ILs plays a decisive role in their performance modulation effects. Smaller cations (such as [Emim]<sup>+</sup>) are more effective than [Bmim]<sup>+</sup> in reducing molecular stacking density, while larger anions (such as [TFSI]) further enhance transparency and flexibility by increasing free volume.192,193 In terms of industrial potential, [Emim] [TFSI] is preferred due to its low commercial cost. A PI-based graphite film with 5.0 wt% ILs achieves a thermal conductivity of 770 W m<sup>-1</sup> K<sup>-1</sup> (1.53 times that of pure PI), and the degree of graphitization increases to 88%.194 In modification, [Bmim][Cl] significantly enhances hydrophilicity through thermally induced phase separation, making it suitable for low-cost film processing.

The functionalized applications of ILs are not limited to polyimide modification; their multifunctional integration in flexible electronic devices (FED) also demonstrates unique value. For example, ILs containing hydrophobic FAP anions modify Nafion membranes, enhancing ionic conductivity by more than three times; self-crosslinking PILs, when used in graphene oxide/carbon nanotube composite films, impart the material with ultra-flexibility (bending radius <1 mm) and high conductivity (>1000 S cm<sup>-1</sup>).<sup>195,196</sup> It is worth noting that ILs also play a key role in the development of soft ionic conductors.<sup>197</sup> Traditional hydrogels, while exhibiting high stretchability (strain >1000%) and biocompatibility, suffer from poor environmental stability, freezing and cracking at low temperatures, and the introduction of conductive fillers often leads to a decrease in transparency (transmittance <50%).<sup>198,199</sup> By introducing inorganic salts (e.g., LiCl) or ILs, new ionic conductors can be developed. Yang developed a biomimetic agarose/polyacrylamide hydrogel containing Li<sup>+</sup>, achieving a tensile strength of 0.22 MPa while maintaining 90% transparency.<sup>200</sup> The Sun group prepared a [Emim][Cl]based double-helix structure ion gel via photopolymerization, exhibiting fast response ( $<100 \text{ m s}^{-1}$ ) and high sensitivity (GF = 2.1).<sup>201</sup> In particular, the plasticizing effect of ILs can break through the performance limits of traditional materials. The [Bmim][NTf<sub>2</sub>]-based ion gel enhances the fracture elongation to 1200% while maintaining 90% transparency by reducing the polymer chain crystallinity, with a triboelectric output density of 12.3  $\mu$ C m<sup>-2</sup>.<sup>202</sup> To address the device interface adhesion issue, Bowen's group prepared ion gels via photopolymerization of acrylic acid in [Bmim][TfO], achieving stable adhesion with the substrate through hydrogen bonds/ van der Waals forces between the ILs polar groups (trifluoromethyl, sulfonyl) and the substrate, with a peel strength >15 N m<sup>-1</sup> at 90% transparency.<sup>203</sup> Advanced design strategies such as double-network, double-crosslinked singlenetwork, and supramolecular assembly have further expanded the performance envelope of IL-based ion gels. For instance, [Emim] TFSI]-based DN gels maintain high fracture energy  $(>5000 \text{ J} \text{ m}^{-2})$  across a wide temperature range, while supramolecular systems featuring hydrogen-bonded nanoscale channels simultaneously achieve high conductivity and transparency. The solvation and plasticization effects of ILs also enable novel energy dissipation mechanisms and dynamic mechanical reinforcement in wearable sensing platforms.<sup>204</sup>

In addition, ILs are also applied in reshaping the paradigm of microelectronics patterning. In the field of scanning probe lithography, PIL films exhibit exceptional field-responsive characteristics. The local electric field of an atomic force microscope tip can induce surface morphology reconstruction of PIL under ultra-low voltages ( $\leq 5$  V), reducing energy consumption by 80% compared to traditional insulating polymers. Through bias voltages (1–5 V) and environmental humidity (30–80% RH) synergistic regulation, precise fabrication of feature sizes ranging from 50 to 200 nm is achieved. This is

attributed to the electro-mechanical effect driven by ion migration, which overcomes the dielectric breakdown limit.<sup>205</sup> *In situ* photoelectron microscopy based on [Emim][TFSI] shows that ion rearrangement and electrostatic response exhibit a critical thickness effect (>3 molecular layers) and a temperature dependence (activation energy  $\approx 0.45$  eV), providing a mechanistic basis for designing patterned ionic circuits.<sup>206</sup>

То address the bottlenecks in functional oxide nanofabrication, RTIL-mediated oxide scanning probe lithography offers a universal solution. Through constructing an IL adsorption layer on substrates such as steel and silicon, the induced voltage is reduced to -2 V, achieving 85 nm resolution for iron oxide patterning, while precisely controlling the  $Fe^{2+}/$ Fe<sup>3+</sup> chemical state ratio and sub-2 nm surface roughness. This technology, leveraging the adaptability of ILs to multi-phase solid surfaces, has been extended to 12 metal substrates, promoting the development of corrosion-resistant arrays.207 microelectrodes and neuromorphic These breakthroughs collectively establish ILs as a core medium for cross-scale patterning. From green direct-write processes replacing toxic solvents, decoding interfacial ion transport, to on-demand customization of oxide electronic properties, the ultimate aim is the integration of three-dimensional microelectronic systems on a single substrate: incorporating ion-conductive paths, memristive oxides, and polymer sensor units into a single process, opening new pathways for advanced packaging and wearable electronics.

In summary, ILs exhibit extraordinary potential as multifunctional modulators in the design and fabrication of next-generation flexible and wearable electronic devices and patterning. By virtue of their unique physicochemical properties, such as low volatility, high ionic conductivity, structural tunability, and strong intermolecular interactions, ILs enable simultaneous enhancement of optical transparency, mechanical flexibility, thermal conductivity, and interfacial adhesion in polymer-based systems. Their incorporation into polyimides and ion gels not only overcomes the intrinsic tradeoffs between transparency and toughness in conventional materials but also facilitates the development of highly stretchable, transparent, and responsive ionic conductors suitable for wearable sensing, energy harvesting, and soft electronics. Advanced molecular designs, including supramolecular networks and dual crosslinking strategies, further unlock new paradigms for IL-integrated material systems with programmable mechanical and electronic properties. These attributes collectively position ILs as a critical platform material for the scalable engineering of multifunctional, durable, and intelligent wearable technologies.

### 6 Conclusions and outlooks

EIMs constitute the foundational pillars of modern information technology, playing a strategic role in enabling advancements in integrated circuits, sensors, display technologies, and communication systems. As the digital era accelerates toward ubiquitous connectivity and intelligent systems, the demand for materials with enhanced electronic, optical, and mechanical performance continues to intensify. While conventional materials such as silicon, gallium nitride, and graphene have driven remarkable progress, limitations in processability, tunability, and multifunctional integration still pose significant constraints. ILs have emerged as promising candidates for nextgeneration material design, offering unprecedented opportunities for fine-tuned modulation and functional enhancement.

This review systematically delineates the multifaceted roles of ILs in advancing EIMs across several dimensions. First, ILs enable the formation of nanometer-scale electric double layers, allowing for ultra-low-voltage, high-efficiency carrier modulation, thereby enhancing the performance of FETs and related architectures. Second, ILs exhibit superior chemical separation capabilities, aiding the purification of electronic-grade materials by efficiently removing ionic and organic contaminants, which is an essential prerequisite for high-performance device fabrication. Third, ILs not only facilitate performance tuning in traditional semiconductors but also unlock new functionalities in frontier domains such as flexible electronics, quantum devices, and energy-efficient storage systems.

Despite these advances, the application of ILs in EIMs remains in its infancy, and several fundamental and practical challenges must be addressed. Chief among them are: (1) the high synthesis cost, ecological safety concerns, and limited recyclability of many ILs, which restrict their scalability and sustainability; (2) the need for comprehensive studies on long-term stability, compatibility, and interfacial interactions between ILs and diverse EIMs platforms, particularly under harsh operational conditions; (3) industrial bottlenecks such as uniform dispersion, large-scale synthesis, and reproducible doping control, which impede their transition from lab-scale demonstrations to commercial integration.

Looking ahead, the transformative potential of ILs in EIMs lies in the convergence of materials chemistry, device engineering, and sustainable manufacturing. Future research should emphasize the development of low-cost, biodegradable, task-specific ILs with programmable molecular and Cross-disciplinary approaches architectures. combining supramolecular design, machine learning-assisted IL screening, and scalable processing techniques will be critical in driving breakthroughs. Furthermore, integrating ILs with emerging material systems, such as 2D semiconductors, perovskites, and organic-inorganic hybrids, may open new frontiers in reconfigurable electronics, neuromorphic computing, and soft robotics. Ultimately, realizing the full potential of ILs in EIMs will not only enable performance upgrades but also reshape the paradigms of material innovation in the digital age.

### Data availability

No primary research results, software or code have been included and no new data were generated or analysed as part of this review.

## Author contributions

Mengyue Li: data curation and writing-original draft preparation. He Bin: conceptualization and methodology, writing-review and editing. Yangyang Jiang: data curation. Ruirui Wang: software and writing-review and editing. Cunliang Gan: data curation. Fengqi Ji: data curation. Yao Li: data curation. Ruixia Liu: supervision, project administration, and acquisition, writing-review and editing.

## Conflicts of interest

All authors declare that they have no conflicts of interest.

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