Review Article

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Innovative synthesis of cobalt-based catalysts using ionic liquids and deep eutectic solvents: A minireview on electrocatalytic water splitting

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Abstract: In recent years, ionic liquids (ILs) and deep eutectic solvents (DESs) have demonstrated significant potential in the field of high-efficiency cobalt-based catalyst preparation due to their unique physicochemical properties. These solvents not only serve as reaction media but also as templating agents and can even directly participate in chemical reactions as reactants, offering a distinct advantage over conventional solvents in enabling multifunctional catalyst design. Through the application of ILs and DESs, researchers have successfully synthesized novel structured and high-performance cobalt-based catalysts that exhibit excellent performance in water splitting reactions. Notably, the tunability of ILs/DESs enables heteroatom doping (P, S, N), revealing synergistic effects on catalytic activity and atom economy, which are rarely discussed in previous literature. This article discusses in detail various synthesis methods, including electrodeposition, solvothermal synthesis, and others, clarifying how ILs/DESs act as both synthetic tools and performance modifiers in the context of electrocatalytic water splitting. Additionally, the article provides an outlook on future research directions, emphasizing the importance of further optimizing catalyst performance, improving synthesis efficiency, and exploring more environmentally friendly synthesis strategies.

Keywords: cobalt-based catalysts, ionic liquid, deep eutectic solvents, water splitting

1 Introduction

Ionic liquids (ILs) are a class of salts that remain liquid at room temperature or near room temperature, typically composed of large organic cations and small anions. Among them, common types of organic cations include imidazolium ions, pyridinium ions, quaternary ammonium ions, etc., while anions cover halide ions, tetrafluoroborate ions, hexafluorophosphate ions, etc. ILs have demonstrated broad application potential in numerous fields [1–3]. Although related research has been relatively in-depth, some limitations still exist (Table 1) [4]. In view of these shortcomings, deep eutectic solvents (DESs) have gradually attracted attention as an alternative.

DESs are two- or three-component eutectic mixtures composed of hydrogen bond acceptors (HBAs) and hydrogen bond donors (HBDs) according to a certain stoichiometric ratio [5], which have similar physicochemical properties to ILs [6–8].

ILs and DESs possess several unique properties, such as:

Negligible volatility, which prevents them from easily volatilizing into the air during reactions and applications, thereby avoiding environmental pollution and safety hazards caused by traditional organic solvents.

Excellent thermal stability, enabling them to remain liquid and non-decomposable over a wide temperature range, making them suitable for high-temperature reaction environments.

Good conductivity, a property that makes them perform prominently in electrochemical fields such as batteries and supercapacitors.

High heat capacity, which plays a crucial role in heat transfer and storage processes.

High designability, allowing researchers to "tailor" ILs with specific functions and properties by changing the types and structures of anions and cations, thus meeting the diverse needs of different fields.

Hydrogen energy, recognized as a clean and low-carbon energy source due to its abundant availability,

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Table 1: Comparison table for DESs and ILs [1,2,5–7]

Feature	DES	IL
Definition	Two- or three-component eutectic mixtures composed of HBAs and HBDs according to a certain stoichiometric ratio	A class of salts that remain liquid at room temperature or near room temperature
Composition	HBDs and HBAs	Cations and anions
Melting point	Have a lower melting point than the individual components	Low melting points
Conductivity	High ionic conductivity, but generally lower than ILs	High ionic conductivity
Viscosity	Tend to have higher viscosity compared to ILs	Lower viscosity compared to DES, facilitating easier handling and application
Toxicity and biodegradability	Often considered less toxic and more biodegradable than ILs	Significant differences
Cost	Generally cheaper to produce	Production higher
Applications	Widely used in green chemistry, including extraction, synthesis, and as solvents for biomolecules	Diverse applications including catalysis, electrochemistry, and as solvents in green chemistry

flexible storage and transportation options, and high heat value, is anticipated to support and sustain the growing demand for and production of environmentally friendly energy solutions. Water splitting is a crucial technological component in the development of clean renewable energy [9]. The reaction is divided into two half-reactions: at the cathode, the hydrogen evolution reaction (HER) occurs to produce hydrogen gas; and at the anode, the oxygen evolution reaction (OER) takes place to generate oxygen (Figure 1). Other elements or substances typically do not participate in these reactions, so only hydrogen and oxygen are generated and released.

Compared to other hydrogen production technologies, water splitting for hydrogen production offers environmental advantages [10]. Regrettably, the sluggish kinetics of HER and OER present significant limitations, leading to excessive overpotentials (the extra voltage beyond the theoretical value needed for electrolysis due to kinetic barriers) and Tafel slope (the change in overpotential with the logarithm of current density, reflecting electrochemical reaction kinetics).

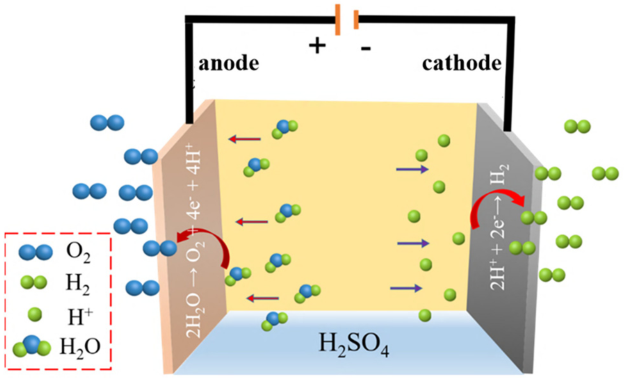

Figure 1: Diagram of water splitting [10].

Electrocatalysts are indispensable in water splitting as they effectively accelerate the kinetics of both the HER and OER. By using meticulously designed electrocatalysts, the efficiency of water splitting can be significantly enhanced, thereby minimizing overpotentials and elevating overall performance. Although precious metal-based electrocatalysts, including Pt, RuO_2, and IrO_2, possess remarkable qualities, their industrial production is limited by scarce reserves and elevated costs [11]. Consequently, the urgent pursuit lies in the advancement of transition metal catalysts. They are resource-rich, adjustable in composition, offer high diversity and cost advantages, and exhibit outstanding corrosion resistance. These transition metal catalysts also demonstrate excellent electrocatalytic activity for water splitting, which is attributed to the characteristics of their d-orbital electrons. In chemical reactions, they can provide empty orbitals to act as electrophilic reagents or lone pairs of electrons to act as nucleophilic reagents, forming intermediates, lowering activation energy, and promoting the electrolysis of water [12].

As a type of transition metal catalyst, cobalt-based catalysts have received considerable attention due to their efficient performance in water splitting. In HER, the absolute value of the Gibbs free energy change (ΔG_H*) for hydrogen adsorption on Co metal is relatively small. Thermodynamically, a metal with a ΔG_H* closer to zero tends to exhibit superior HER performance. For OER, the higher oxidation states of cobalt, such as Co(IV), can effectively serve as active centers to promote the OER, which is beneficial for the formation of metal hydroxides and facilitates the chemical desorption of OH groups [13–16]. There are many methods for preparing cobalt-based catalysts, such as electrodeposition [17,18], solvent thermal [19], etc. Despite the availability of various synthesis strategies, cobalt-based nanomaterials often lag behind noble metal catalysts in terms of catalytic performance and stability. To overcome these limitations, researchers have adopted ILs and DESs to optimize the synthetic process. The use of these solvents can modify the structure and morphology of cobalt-based materials, thereby contributing to enhanced catalytic efficiency.

This review systematically discusses the applications of ILs/DESs as multifunctional media (reaction solvents, templating agents, reactants) in the synthesis of cobalt-based catalysts, and how their unique properties directly enhance the performance of electrocatalytic water splitting. It is divided into three parts. The first part introduces the advantages of using ILs and DESs to prepare novel structured and superior performance cobalt-based catalysts. The second part provides a detailed review for preparing electrocatalytic water splitting cobalt-based catalysts using ILs and DESs by electrodeposition, solvothermal approaches, and so on. In the concluding portion, we not only encapsulate the key points of the review but also venture to forecast the emerging trends in the advancement of IL/DES-enabled cobalt-based catalysts, highlighting their potential impact on future research directions within this field. Unlike previous works that solely focus on catalytic activity, this study integrates mechanistic insights, synthetic efficiency, and green chemistry principles, offering a holistic perspective on the potential of ILs/DESs in electrochemical applications.

2 Synthetic strategies for high-performance cobalt-based catalysts via ILs and DESs in electrocatalytic water splitting

2.1 Electrodeposition technology

Electrodeposition technology is an effective method for preparing catalysts by adding substances such as metal ions into an electrolyte and obtaining the target product through the action of an electric field (Figure 2) [20,21]. By adjusting the parameters of the electrolyte, it is possible to control the structure and properties of the deposited material. The solvent in the electrolyte is usually water or organic solvents. Water is the most commonly used solvent due to its environmental friendliness, low cost, and easy availability. However, under certain circumstances, organic solvents such as acetonitrile, *N*,*N*-dimethylformamide (DMF), and *N*,*N*-dimethylacetamide are also employed to achieve better electrochemical properties or specific crystal structures. However, traditional electrolytes have a series of issues.

Narrow electrochemical windows, which mean many electrodeposition reactions requiring high potential driving forces (e.g., deposition of highly reactive metals, synthesis of complex compounds) cannot proceed.

Volatility, leading to changes in electrolyte composition over time (increased solute concentration after solvent evaporation), which affects the repeatability and stability of the electrodeposition process.

Temperature limitations, restricting the application of electrodeposition technology in extreme environments (e.g., high-temperature metallurgy, preparation of low-temperature energy storage devices).

Strong corrosiveness, specifically causing corrosion and damage to equipment, increasing maintenance costs, posing safety hazards, and affecting the purity and performance of deposited materials [22–24].

In the preparation of transition Co-based catalysts, ILs and DESs are increasingly being used as electrolytes. This is attributed to their unique properties compared to traditional water or organic solvents, such as good conductivity, wide electrochemical windows, environmental friendliness, mild conditions, and a wider range of operating temperatures (Table 2). Murchite et al. investigated the electrical conductivity and thermal stability of *N*,*N*-dimethylethanolammonium-based ILs and found that they remained stable at high temperatures (323 K) with a conductivity >5 mS cm^{-1}. The wide electrochemical windows of ILs (e.g., [BMIM][PF_6] exhibits a window of 4.5 V) can avoid side reactions (such as water decomposition) at high potentials, thereby reducing corrosion of the stainless steel surface caused by OERs. Experiments show that at a potential of 2.5 V vs SCE, the corrosion rate of stainless steel in the ILs system is 0.08 mm/year, which is only 32% of that in an aqueous solution (0.25 mm/year) [25]. Electrochemical stability of ILs and DESs makes them well-suited for the electrodeposition process, which helps maintain the morphology and uniformity of the catalysts. Furthermore, ILs and DESs can remain stable and are less prone to reacting with other substances, which benefits the preservation of the catalysts' chemical purity and stability. Additionally, due to their high viscosity, ILs and DESs can be used to regulate the morphology of products, leading to porous metal nanostructures. Using ILs and DESs as electrolytes can also result in more uniform particle distribution and reduced waste. The catalytic performance of cobalt-based catalysts obtained by electrodeposition method has been comprehensively summarized in Table 3.

Although ILs and DESs may have a high cost, this investment can be justified considering their benefits in

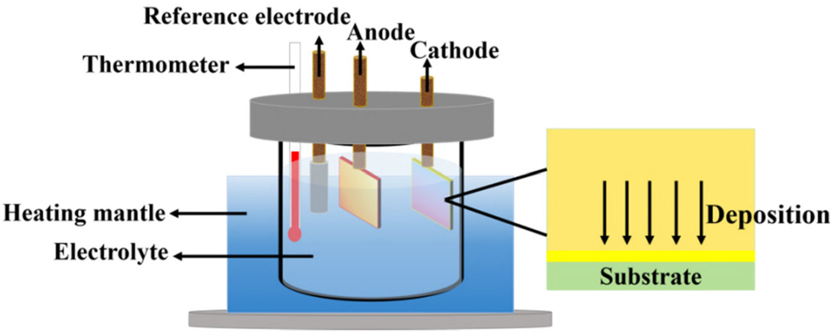

Figure 2: Diagram of electrodeposition technology [20,21].

improving catalyst performance and longevity. The choice of solvent should be based on specific application requirements and objectives.

Using DESs as electrolytes, the addition of transition metals allows for the electrolytic production of transition metal compounds. By adjusting the composition of the DESs, it is possible to control the structure and performance of the catalysts. The use of ChCl/malonic acid DES with a small percentage of water as the electrolyte for electrodepositing cobalt resulted in an electrodeposited layer with a unique plate-like morphology of Co nanoparticles from cobalt salt. The structured nature of DES can influence the nucleation and growth of cobalt crystals, favoring the formation of flat planes over other shapes. The addition of a small percentage of water reduced the viscosity of the ChCl/malonic acid DES, while altering the local structure around the cobalt ions in the DES. Water content can affect reduction of cobalt salt and deposition kinetics of electrodeposited layer, which might favor the development of a plate-like morphology and the quality of the electrodeposited films. The resulting structure consisted of well-separated nanoclusters of cobalt on the surface of a dense graphite sheet. Despite the absence of stabilizing agents, the cobalt nanoparticle clusters had a size range of approximately 50–80 nm. The reason is possible to that the combination of ChCl and malonic acid in DES creates a complex hydrogen-bonding network that can stabilize specific crystal facets of cobalt during electrodeposition, promoting the growth of plate-like structures. After the catalyst is prepared, residual ILs/DESs are thoroughly removed by centrifugal washing (8,000 rpm, 10 min) and vacuum drying (80°C, 12 h). The cobalt nanoparticles displayed remarkable HER performance, achieving a current density of 10 mA cm^{-2} with an overpotential of 350 mV and a Tafel slope of 76 mV dec^{-1} in 1 M KOH solution [26].

To enhance the catalytic effects of cobalt-based catalysts, other metal salts are incorporated into ILs and DESs, thereby forming alloys, such as Ni–Co [27], Co–Cu [28], Ni–Co–Sn [29], and Zn–Co [30]. There are various methods for preparing cobalt-based alloys, including molten salt electrolysis and mechanical alloying, among others. Given that DESs have excellent solubility for a variety of metal salts, using DES as an electrolyte for electrodeposition is an effective strategy for producing cobalt-based alloys. The solubility and electrochemical behavior can be adjusted by altering the components of the DES, enabling precise control over the structure and composition of the alloy. Cobalt alloys electrodeposited in DES typically exhibit

Table 2: Advantages of ILs and DESs in electrodeposition of transition metal catalysts over water or organic solvents [22–25]

Aspect	ILs	DESs	Water or organic solvents
Chemical stability	High	High	Moderate
Thermal stability	High	High	Moderate
Electrochemical window	Broad	Broad	Narrow
Solubility	Strong	Strong	Moderate
Environmental friendliness	Low volatility, recyclable	Low volatility, recyclable	High volatility, difficult to recycle
Cost	Relatively high	Relatively low	Relatively low
Conductivity	Good	Good	Moderate
Safety	Non-toxic, non-flammable	Non-toxic, non-flammable	Toxic, flammable
Operating temperature range	Wide (−40 to 300°C)	Wide	Narrow
Impact on catalysts	Controllable dissolution and stability	Controllable dissolution and stability	Significant impact

Table 3: Water splitting performance of cobalt-based catalysts prepared by electrodeposition technology

Catalyst	Applied IL/DES	Catalytic performance								Refs.
		HER			OER			Overall water splitting		
		Electrolyte	η (mV)@Current density (mA cm^{-2})	Tafel slope (mV dec^{-1})	Electrolyte	η (mV)@Current density (mA cm^{-2})	Tafel slope (mV dec^{-1})	Electrolyte	Potential (V) @Current density (mA cm^{-2})	
Co	ChCl/malonic acid	—	—	—	1 M KOH	350@10	76	—	—	[26]
$Ni_{88.7}Co_{11.3}$	Ethylammonium nitrate	—	—	—	1 M KOH	480@10	93.3	—	—	[27]
$Ni_{77.2}Co_{22.8}$	Ethylammonium nitrate	—	—	—	1 M KOH	510@10	112.1	—	—	[27]
$Ni_{64.4}Co_{35.6}$	Ethylammonium nitrate	—	—	—	1 M KOH	300@10	83.6	—	—	[27]
$Ni_{62.0}Co_{38.0}$	Ethylammonium nitrate	—	—	—	1 M KOH	420@10	93.5	—	—	[27]
$Ni_{58.6}Co_{41.4}$	Ethylammonium nitrate	—	—	—	1 M KOH	460@10	88.6	—	—	[27]
$Ni_{51.9}Co_{48.1}$	Ethylammonium nitrate	—	—	—	1 M KOH	190	71.3	—	—	[27]
$Ni_{30.9}Co_{69.1}$	Ethylammonium nitrate	—	—	—	1 M KOH	340	68.9	—	—	[27]
Co	Ethylammonium nitrate	—	—	—	1 M KOH	400	107.4			[27]
$Co_{59}Cu_{41}$	Ethylammonium nitrate	0.5 M H_2SO_4	342	103	—	—	—	—	—	[28]
Ni–Co–Sn	ChCl/EG	—	—	—	1 M KOH	—	121	—	—	[29]
Co	ChCl/EG	—	—	—	1 M KOH	372@10 578@100	—	—	—	[30]
Zn_3Co_{97}	ChCl/EG	—	—	—	1 M KOH	333@10 524@100	108.2 ± 0.74	—	—	[30]
$Zn_{96}Co_4$	ChCl/EG	—	—	—	1 M KOH	355@10 600@100	—	—	—	[30]
Co-S/NF	ChCl/EG	1 M KOH	124@100	65	1 M KOH	322@100	66.4	30 wt% KOH	1.72 V	[31]
NiCoP	Methyltriphenylphosphonium bromide/EG	1 M KOH	93@10	48	—	—	—	—	—	[32]
$NiCo_xS_y$/NF	ChCl/EG	1 M KOH	65	62.5	1 M KOH	300@20	109	1 M KOH	1.57@10	[33]

superior dispersibility, which means more active sites and thus enhanced catalytic efficiency. The unique properties of DESs can promote the growth and formation of specific crystal facets, leading to the creation of plate-like or other non-spherical structures with high activity, which are particularly advantageous for catalytic reactions. Additionally, since cobalt alloys electrodeposited in DES often possess better dispersion and higher activity, employing this strategy can enhance both the yield and quality of the alloys.

Cobalt salt, nickel salt, and tin salt are introduced into ChCl/EG DES. Ni–Co–Sn alloy were gotten by electrodeposition, which showed high corrosion current density and exchange current density potential, indicating that the Ni–Co–Sn alloy with high performance and stability was a good candidate for HER [29]. Zinc, cobalt, and zinc–cobalt coatings can also be obtained using electro-deposition methods with ChCl/EG DES. By altering the concentration of Zn^{2+} and Co^{2+} ions, crystalline deposits with precisely controlled compositions and morphologies were achieved, exhibiting different electrocatalytic HER activities in alkaline media (Figure 3). An increase in the cobalt content within the coating had a positive impact on the HER performance [30].

In the context of electroplating processes, the introduction of an appropriate amount of sulfur sources enables the direct electrodeposition of cobalt sulfide. Within the aforementioned DES-metal salt electrolyte system, incorporating a non-metallic source can yield catalysts such as cobalt sulfide and cobalt phosphide. The preparation of porous S-doped Co–S films grown on nickel foam (Co–S/NF) has been successfully achieved through a one-step electrodeposition approach using DES as the electrolyte. DES had the capability to form stable Co(ɪɪ)–Cl complexes with cobalt ions, which could coordinate with Co(ɪɪ)–thiourea (TU) complexes to precisely control the generation of Co–S complexes (Figure 4). Co–S/NF exhibited features of highly exposed active sites and strong structural integrity, demonstrating excellent water splitting performance, particularly at high current densities, requiring only 1.72 V to

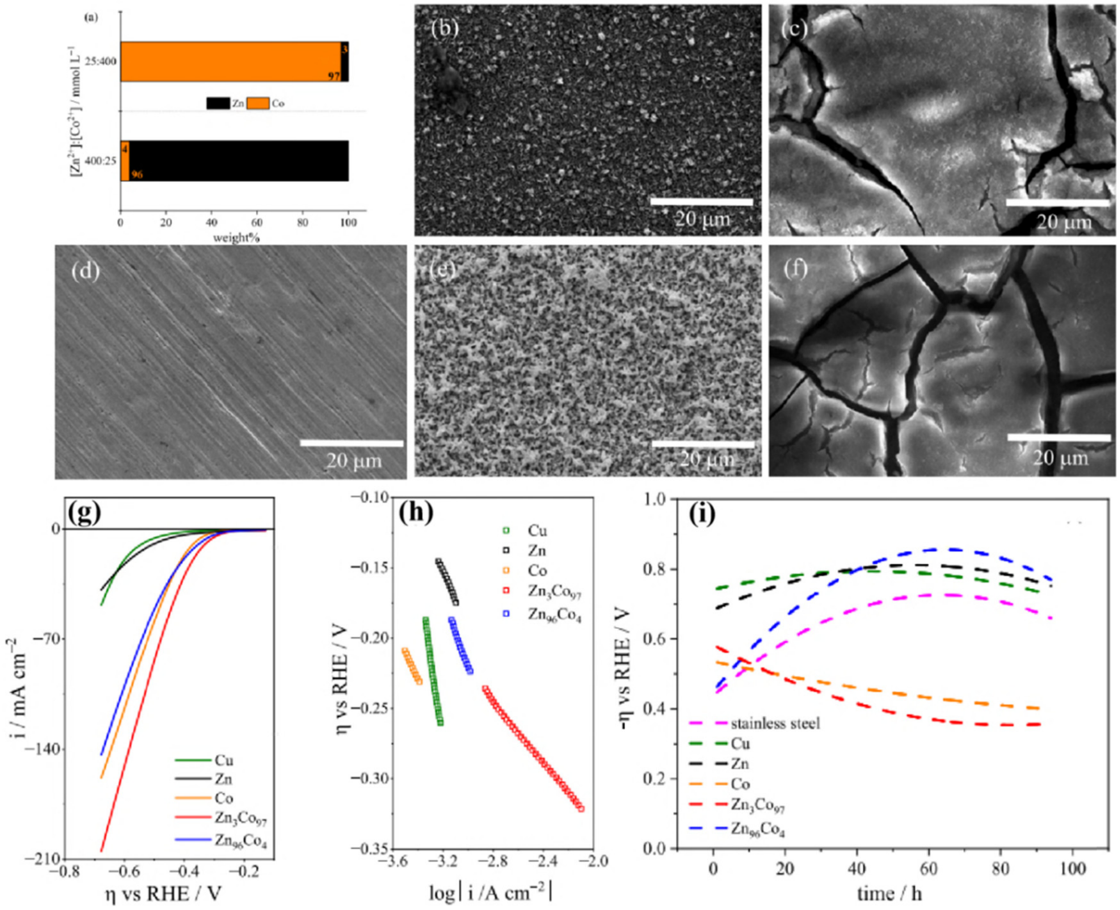

Figure 3: Metallic composition (a), the SEM images of Cu substrate (b), Cu/Zn (c), Cu/Co (d), Cu/$Zn_{96}Co_4$ (e), and Cu/Zn_3Co_{97} (f), polarization curves carried out with different catalysts (g), the corresponding Tafel slopes (h), and electrochemical stability tests of the catalysts (i) [30].

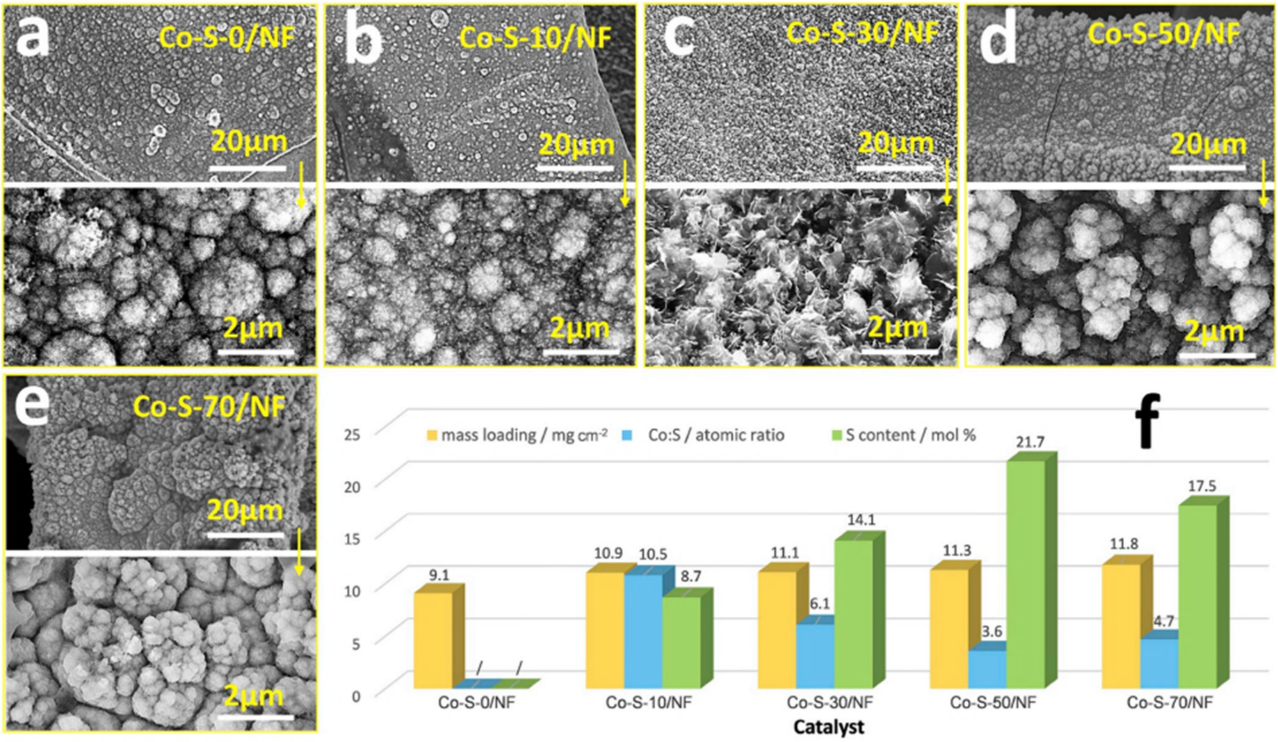

Figure 4: (a)–(e) FE-SEM images of the as-prepared Co–S–x/NF (x = 0, 10, 30, 50, and 70) with different TU feed concentrations. (f) The corresponding mass loading, atomic ratio of Co/S, and S doping content [31].

achieve a large current density of 500 mA cm^{-2} in 30 wt% KOH solution. S doping enhanced charge and mass transport while promoting catalysis kinetics by increasing the electrochemical active area and creating structural defects [31]. These defects, counterintuitively, serve to improve the catalyst's performance by providing additional active sites and facilitating electron transfer, a phenomenon consistent with the theory of defect chemistry in materials science. The synergy between the controlled release of sulfur species from the DES medium and the unique electrochemical properties of the DES electrolyte contributes to the superior electrocatalytic activity observed in the Co–S/NF composites.

Moreover, ILs and DESs can also be used to prepare bimetallic sulfides and phosphides. Compared to single-metal sulfides, bimetallic sulfides exhibit higher electrical conductivity. The mixed valence states of the metal ions and the cooperative electronic interactions increase their reactivity, revealing great potential. Bimetallic sulfides and phosphides can be readily obtained through the simultaneous addition of multi-metal sources and non-metallic sources in IL and DES electrolytes.

Wang research group meticulously designed a methyltriphenylphosphonium bromide/ethylene glycol DES and utilized a potentiostatic method to electrodeposit a nickel–cobalt phosphide (NiCoP) film onto the surface of carbon cloth (CC). The formation of this film followed a diffusion-controlled three-dimensional instantaneous nucleation and growth mechanism, ensuring the quality of the film while highlighting the dominant role of the diffusion process. Initially, raw molecules diffused freely in the solution or vapor phase and then rapidly aggregated under suitable conditions to form primary crystal nuclei. Subsequently, these nuclei continued to grow through precise processes such as surface diffusion and material adsorption, ultimately shaping a structurally complete film. The synergy between the DES's unique hydrogen-bonding network and the carefully controlled deposition potential fosters a uniform nucleation and growth process, resulting in a dense and conformal coating that optimizes the electrochemical performance. Additionally, the presence of phosphorus introduces electronic modifications to the Ni–Co lattice, enhancing the electrical conductivity and stability of the catalyst, which aligns with the principles of d-band center theory in electrocatalysis. Furthermore, the choline chloride-ethylene glycol DES's ability to fine-tune the reduction potential of nickel and cobalt salts contributes to the precise control over the composition and structure of the NiCoP film, thereby amplifying its catalytic activity. This NiCoP film demonstrated outstanding HER activity, with an η_{10} value of only 93 mV and a Tafel slope as low as 48 mV dec^{-1} in a 1 M KOH [32], reflecting its exceptional electrocatalytic efficiency. In a similar vein, Zeng et al. have successfully synthesized $NiCo_xS_y$ by electrolyzing a mixture containing $NiCl_2$, $CoCl_2$, and TU within a ChCl/EG DES. This structure exhibited impressive water splitting performance, achieving a current density of 10 mA cm^{-2} with a low overpotential of 1.57 V [33]. This achievement underscores the potential of DESs in tailoring the local electrochemical environment to facilitate the formation of desired intermetallic phases and dopant distributions, which are crucial for enhancing the catalytic performance of transition metal compounds in water splitting reactions. The combination of precise compositional control and the inherent properties of DESs offers a promising route for the rational design of advanced electrocatalysts tailored for energy conversion applications. Using either DESs or ILs as electrolytes, it is possible to incorporate metals capable of forming alloys with cobalt, such as iron, nickel, chromium, tungsten, molybdenum, copper, etc., according to specific requirements. This enables the controllable enhancement of catalyst performance, making it suitable for various industrial applications.

2.2 Solventothermal technology

Solventothermal synthesis is a chemical synthesis technique carried out under high temperature and pressure conditions within a closed system, where the use of solvents facilitates chemical reactions at temperatures lower than those traditionally required for high-temperature reactions [34]. The advantage of this method lies in its ability to achieve high-temperature reaction conditions at lower external temperatures, typically due to the natural increase in internal pressure within the sealed system rather than externally applied pressure. This approach enhances the purity and crystallinity of the products because the reactions take place in a more controlled environment, reducing the occurrence of side reactions and allowing for the formation of more complete crystal structures. By precisely controlling parameters such as temperature, pressure, and time, the reaction rate and product morphology can be controlled, allowing for precise control over the properties of the product. Although high-purity products and large-sized crystals can be synthesized in a short time, solventothermal synthesis faces challenges such as high equipment costs and complex operations [35]. Moreover, strict requirements for reaction conditions and factors such as the solubility and kinetics of reactants may affect the outcome of the reaction. Therefore, when conducting solventothermal synthesis, it is necessary to carefully select reaction conditions and solvent systems to ensure the effectiveness and reproducibility of the synthesis process [36,37]. The performance of cobalt-based catalysts prepared by solvothermal method for water splitting is shown in Table 4.

In the preparation of transition metal catalysts via the solvothermal method, commonly used solvents include water, alcohols (such as methanol, ethanol, isopropanol), organic acids (such as acetic acid, formic acid), ketones (such as acetone), esters (such as ethyl acetate), amines (such as pyridine, triethylamine), and other polar aprotic solvents (such as nitrile, DMF, dimethylsulfoxide, etc.). The choice of solvent depends on the desired reaction conditions, target product, and the solubility of reactants. In recent years, ILs and DESs have gained special attention as solvents in solvothermal reactions. Compared to traditional solvents, they offer the following advantages:

Broad liquid temperature range: ILs and DESs are liquid at room temperature or close to it, providing a wider operating temperature window.

High thermal stability: Both ILs and DESs typically possess high thermal stability, allowing their use at elevated temperatures without decomposition.

Excellent electrochemical stability: They are stable across a wide pH range, suitable for reactions related to electrochemistry.

Good solubility: Capable of dissolving various inorganic salts and organic compounds, applicable to a variety of chemical reactions.

Adjustable physical and chemical properties: By altering the composition of ILs and DESs, their polarity, dielectric constant, and other properties can be adjusted to meet different reaction requirements.

Low volatility: Their low volatility reduces evaporation losses during high-temperature reactions, facilitating continuous operation and catalyst recovery. Moreover, many ILs and DESs are non-toxic or low-toxic, renewable, and have a smaller environmental impact.

Recyclable and reusable: ILs and DESs can be recovered and reused multiple times through simple separation steps, reducing costs and waste generation. These characteristics make ILs and DESs ideal solvent choices, especially in catalytic reactions requiring mild conditions, high selectivity, and efficiency.

However, their cost and synthetic complexity are also factors to consider. When selecting solvents, one should take into account the specific needs of the reaction, cost-effectiveness, and sustainability.

Monometallic (Co, Ni, Fe) and bimetallic (FeCo, NiCo, NiFe) hydroxides were successfully synthesized by adding 1-butyl-3-methylimidazolium tetrafluoroborate ($[BMIM]BF_4$) IL and corresponding metal salts to water and conducting a

Table 4: Water splitting performance of cobalt-based catalysts prepared by solventothermal technology

Catalyst	Applied IL/DES	Catalytic performance								Refs.
		HER			OER			Overall water splitting		
		Electrolyte	η (mV)@Current density (mA cm^{-2})	Tafel slope (mV dec^{-1})	Electrolyte	η(mV)@Current density (mA cm^{-2})	Tafel slope (mV dec^{-1})	Electrolyte	Potential (V)@Current density (mA cm^{-2})	
CoFe	[PMIM]BF$_4$	—	—	—	1 M KOH	350@10	57.5	—	—	[38]
CoNi	[PMIM]BF$_4$	—	—	—	1 M KOH	420@10	98.7	—	—	[38]
N,P-C/NiCoP	[BMIM]PF$_6$	0.5 M H$_2$SO$_4$	108@10	68	—	—	—	—	—	[39]
N,P-C/NiCoP	[BMIM]PF$_6$	1 M KOH	128@10	70	—	—	—	—	—	[39]
N,P-C/NiCoP	[BMIM]PF$_6$	1.0 M PBS	108@10	82	—	—	—	—	—	[39]
NiCo$_2$S$_4$	PEG 200/TU	—	—	—	1 M KOH	337@10	64	—	—	[40]
CoNi$_2$S$_4$/CC	NiCl$_2$·6H$_2$O/ CoCl$_2$·6H$_2$O/TU	1 M KOH	30@10 155@50	117.2	1 M KOH	153@10 372@100	67.1	1 M KOH	1.42@10 1.86@100	[41]
NBF–CoSe/ Mo$_2$CT$_x$	[EMIM][BF$_4$]	0.5 M H$_2$SO$_4$	70	30	—	—	—	—	—	[42]
NBF–CoSe/ Mo$_2$CT$_x$	[EMIM][BF$_4$]	1 M KOH	81	29	—	—	—	—	—	[42]

one-step rapid reaction under alkaline conditions. This IL plays a crucial role in this synthesis process; it serves not only as a reaction medium but also participates in the coordination and dispersion of metal ions, thereby influencing the morphology and structure of the hydroxides. The anion of the IL (e.g., BF_4^-) can form coordination bonds with metal ions, which aids in the uniform dispersion of metal ions in solution, promoting the formation of hydroxide nanoparticles. Additionally, the steric and charge effects of the IL can regulate the growth and path of metal hydroxides, leading to the preferential growth and thus affecting the crystal structure and morphology of the final products. All the prepared hydroxides exhibited excellent performance in the OER. In particular, the CoFe hydroxide and CoNi hydroxide showed overpotentials of 350 and 420 mV, respectively, when the current density was at 10 mA cm^{-2} [38]. These materials hold significant potential for applications in the field of electrocatalysis, particularly in areas related to energy conversion and storage, such as hydrogen production through water electrolysis.

Using 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM]PF$_6$) as an auxiliary agent, nitrogen and phosphorus-doped carbon/nickel cobalt phosphide (N,P-C/NiCoP) composites were successfully prepared. Density functional theory analysis indicated that the doping of nitrogen and phosphorus in the carbon-based materials facilitated electron transfer and increased active sites. The templating effect of this IL endowed the material with a unique wrinkled surface structure, significantly enhancing its specific surface area to five times that of the undoped sample. N,P-C/NiCoP exhibited excellent HER performance, with η_{10} values of 108, 128, and 108 mV under acidic, alkaline, and neutral conditions, respectively [39].

Mu and other researchers developed an innovative DES composed of polyethylene glycol (PEG)200 and TU, and successfully synthesized various sulfides, including CoS$_2$, NiS$_2$, and Ni$_2$CoS$_4$, through a simple solvothermal technique. In this method, DES had significant advantages. First, the use of DES as a structure-directing agent effectively controlled the micro-morphology of the products. For example, NiCo$_2$S$_4$ exhibited a unique urchin-like micro/nanostructure with uniformly connected nanorods forming a network. The components in DES influence the aggregation state and solubility of the precursors through intermolecular forces like hydrogen bonding and van der Waals interactions, guiding the morphological development of sulfides. This structural directing effect helps to form specific microstructures, such as the sea urchin-like micro/nanostructures of NiCo$_2$S$_4$, which may provide more active sites and shorter ion transport pathways, thereby enhancing the electrochemical performance. Second, the DES also acted as a sulfur source, simplifying the reaction process, reducing the likelihood of side reactions, and lowering the overall preparation cost. Under solvothermal conditions, the heat stability and solvent effects provided by DES contribute to optimizing the thermodynamic and kinetic conditions of the reaction, enabling the formation of sulfides under relatively milder conditions, reducing unnecessary side reactions, and improving the purity and performance of the products. The synthesized $NiCo_2S_4$ demonstrated good oxygen evolution activity, with an overpotential of 337 mV and a Tafel slope of 64 mV dec^{-1} [40].

Wang et al. utilized $NiCl_2{\cdot}6H_2O/CoCl_2{\cdot}6H_2O$/TU DES to grow $CoNi_2S_4$ nanosheets on CC substrates through solvothermal synthesis (Figure 5a). This method allowed for an even coverage of the CC with the DES due to its strong adhesive properties and liquid state under ambient temperature conditions. The coupling of the $CoNi_2S_4$ nanosheets with the CC substrate enhanced electron transport efficiency while preventing the catalyst from aggregating and corroding during catalysis processes. The self-supported $CoNi_2S_4$/CC exhibited excellent HER activity (with an overpotential of 155 mV at 50 mA cm^{-2} and 30 mV at 10 mA cm^{-2}) and OER activity (with an overpotential of 372 mV at 100 mA cm^{-2} and 153 mV at 10 mA cm^{-2}). Additionally, this material demonstrated good performance and stability during the electrolysis of seawater (Figure 5b) [41].

Zhang et al. have developed a novel composite material called NBF–CoSe/Mo_2CT_x, which includes B, N, and F-doped CoSe and Mo_2CT_x MXene. This material was synthesized using a hydrothermal process with [EMIM][BF_4], urea, and $Co(NO_3)_2{\cdot}6H_2O$ (Figure 5). During this process, the elements B, N, and F from the IL were introduced into the layered double hydroxide (LDH) nanosheets, which were then calcined to form the final NBF–CoSe/Mo_2CT_x composite. This composite material exhibited enhanced HER activity across a range of pH levels, requiring overpotentials of just 70 and 81 mV to achieve a current density of 10 mA cm^{-2} in 0.5 M H_2SO_4 and 1 M KOH, respectively. Theoretical studies indicated that B, N, and F doping creates additional active sites and improves electronegativity, leading to enhanced proton adsorption capabilities. The combination of Se vacancies, heteroatom doping, and the Mo_2CT_x structure contributed to the excellent HER activity observed in this material [42].

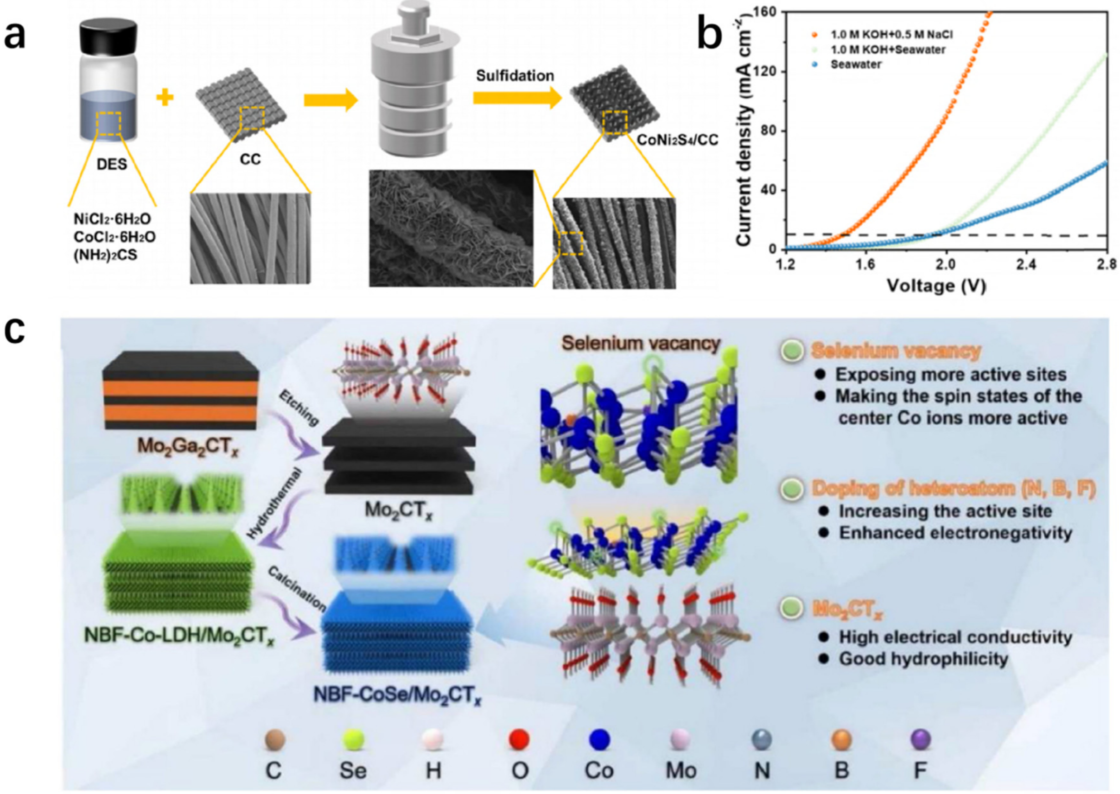

Figure 5: Schematic illustration of the synthesis procedures of $CoNi_2S_4$/CC (a), LSV curves for the $CoNi_2S_4$/CC@$CoNi_2S_4$/CC coupled electrolyzer in different electrolytes (b) [41]. Synthetic process for fabricating NBF-CoSe/Mo_2CT_x (c) [42].

Table 5: Water splitting performance of cobalt-based catalysts prepared by hot injection technology, inkjet printing technology, and microwave-assisted technology, respectively

Catalyst	Applied IL/DES	Catalytic performance								Refs.
		HER			OER			Overall water splitting		
		Electrolyte	η (mV)@Current density (mA cm^{-2})	Tafel slope (mV dec^{-1})	Electrolyte	η (mV)@Current density (mA cm^{-2})	Tafel slope (mV dec^{-1})	Electrolyte	Potential (V) @Current density (mA cm^{-2})	
CoFe-LDH	ChCl/urea	—	—	—	0.5 M KOH	—	—	—	—	[46]
$CuCo_2S_4$	Cobalt(II) bis(*n*-butylpyridine) tetrachlorocuprate(II)	—	—	—	1 M KOH	230@10	211	—	—	[47]
CoP/ carbon fiber	$[BMIM]PF_6$	0.5 M H_2SO_4	97@10	50.2	—	—	—	—	—	[50]
NiP/ carbon fiber	$[BMIM]PF_6$	0.5 M H_2SO_4	102@10	53.3	—	—	—	—	—	[50]
FeP/ carbon fiber	$[BMIM]PF_6$	0.5 M H_2SO_4	111@10	63.4	—	—	—	—	—	[50]
MoP/ carbon fiber	$[BMIM]PF_6$	0.5 M H_2SO_4	87@10	49.1	—	—	—	—	—	[50]
Co_2P/CNT	$[P_{66614}]_2CoCl_4$	0.5 M H_2SO_4	135@10	58	—	—	—	—	—	[54]

2.3 Specific technology

2.3.1 Hot injection technology

The hot injection technology is a common technique for preparing nanomaterials and quantum dots, involving steps such as precursor solution preparation, heating, rapid injection into a hot solvent, and product formation [43,44]. This technology offers advantages such as fast reaction, controllable size, high crystallinity, and versatility, allowing for the precise synthesis and customization of nanomaterials. In brief, the hot injection technology is a rapid, controllable, and versatile approach to nanomaterial fabrication, providing an important tool for the science and application fields of nanomaterials [45].

Researchers utilized the hot injection technology to prepare CoFe LDHs with large interlayer spacing. They added measured quantities of $CoCl_2·6H_2O$ and $FeCl_3·6H_2O$ to a ChCl/urea DES and then heated the mixture. Water was then rapidly injected in increments. The urea decomposed to produce hydroxide ions (OH^-), which reacted with the metal ions to form the LDH structure. Controlling the speed of nucleation was key, and the swift addition of water helped in the uniform growth of the crystals. X-ray diffraction (XRD) analysis revealed that the maximum interlayer spacing of the LDH reached 11.3 Å. Fourier-transform infrared spectroscopy results showed that the molecules intercalated within the layers were decomposition products of the DES, indicating that the DES played a role not only as a solvent but also in the formation of the interlayer composition of the LDH, beneficial for OER (Table 5) [46]. Taubert and colleagues heated a type of IL containing cobalt and copper ions, where the anions and N-butylpyridinium ions served as the anions and cations, respectively. After heating, they rapidly injected hexamethyldisilathiane $(TMS)_2S$ to obtain nanoflower-like $CuCo_2S_4$ with a lower onset potential and improved durability during the OER (Figure 6 and Table 5) [47].

2.3.2 Inkjet printing technology

Inkjet printing technology is a simple and highly controllable technology for the preparation of nanomaterials. It employs a nozzle to eject a solution or suspension of nanomaterials onto a substrate, offering advantages such as strong size controllability, high-throughput production, low cost, and applicability to a variety of nanomaterials. This technology serves as an important tool in the field of nanomaterial science and applications [48,49].

Employing inkjet printing technology, in conjunction with $[BMIM]PF_6$ IL and metal salt solutions, researchers

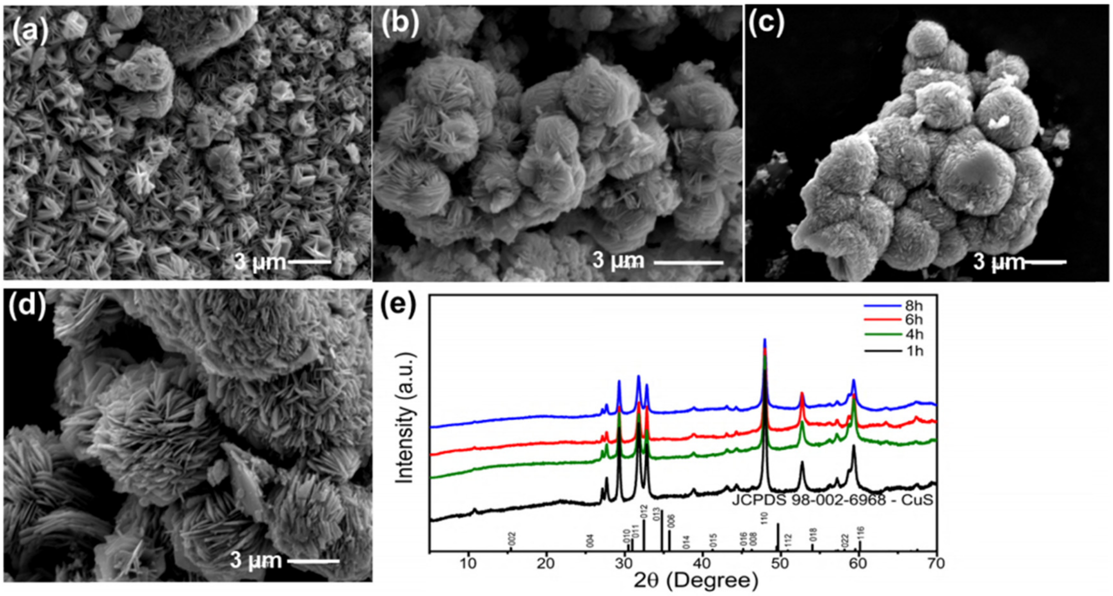

Figure 6: SEM images of the synthesized CuS particles at 160°C at different reaction times: 1 (a), 4 (b), 6 (c), and 8 h (d), their respective XRD patterns (e) [47].

successfully fabricated metal phosphide (CoP, MoP, FeP, NiP)/carbon fiber composites that exhibited excellent performance across a full pH range. In the reaction, the IL served as both a phosphorus source and a carbon source. The *in situ* generated carbon nanolayers displayed abundant catalytic active sites for HER, enhancing the electron transfer rate. Additionally, the presence of the *in situ* carbon nanolayers protected the transition metal phosphide nanoparticles from corrosion, thereby improving the material's stability. Taking the CoP/carbon fiber composite as an example, in 0.5 M H_2SO_4, this catalyst required only a 97 mV overpotential to achieve a current density of 10 mA cm^{-2}, with a low Tafel slope of 50.2 mV dec^{-1} (Table 5) [50].

2.3.3 Microwave-assisted technology

Microwave-assisted synthesis is a technique that utilizes microwaves as an energy source to accelerate the chemical reaction process. In this approach, microwaves are used to directly heat the reaction mixture, as opposed to the indirect heating of water baths or oil baths through heating the reaction vessel, which is the traditional method. This direct form of heating can significantly speed up the reaction rate and allows for reactions to occur at lower temperatures, potentially leading to higher selectivity and yield. Moreover, microwaves can influence the reaction pathways, sometimes enabling different reaction outcomes or new reactions. By adjusting microwave parameters and reaction conditions, the size and morphology of the nanomaterials can be precisely controlled, providing an important tool for nanoscience and applications [51,52]. When synthesizing transition metal catalysts using microwave-assisted methods, the choice of solvent is crucial. An ideal solvent should efficiently absorb microwave energy while also dissolving the reactants, allowing the reaction to proceed smoothly. ILs and DESs are frequently used as solvents in this synthetic approach due to their unique physicochemical properties (Table 5).

Our research group employed the microwave technology, utilizing the quaternary phosphonium chloride ($[P_{4444}]Cl$) IL as both a medium and a template, to synthesize a series of nickel-based catalysts with high catalytic performance. This demonstrated that quaternary phosphonium salts could serve as an excellent phosphorus source [53]. Based on this work, the Li research group used $[P_{6614}]_2CoCl_4$ as both the phosphorus and cobalt source, mixed it with CNT, and synthesized Co_2P/CNT via the microwave technology. The experimental results indicated that $[P_{6614}]_2[CoC_{l4}]$ could form Co_2P without the addition of other reagents, and the incorporation of CNT could enhance the electrical conductivity and facilitate the formation of cobalt phosphide. In acidic solutions, Co_2P/CNT exhibited excellent HER activity. Taking the microwave-synthesized Co_2P/CNT as an example, it had an onset overpotential of only 80 mV and a Tafel slope of 58 mV dec^{-1} (Table 5) [54]. Mechanistically, microwave technology plays a pivotal role in the synthesis process. The nonthermal effects of microwaves can rapidly activate the reactants, promoting the decomposition of $[P_{6614}]_2[CoCl_4]$ into Co_2P. The introduction of carbon nanotubes enhances the electron transfer efficiency, thereby increasing the overall catalytic activity. Additionally, the high surface area of carbon nanotubes provides more active sites for the dispersion of cobalt phosphide, further improving the performance of the catalyst. These factors work together to make Co_2P/CNT exhibit excellent catalytic performance in the HER.

3 Summary and outlook

This article delves into the synthesis of cobalt-based catalysts using ILs and DESs, highlighting their advantages over traditional technologies. ILs and DESs have proven to be superior in crafting cobalt-based catalysts with innovative structures and enhanced performance, particularly in terms of activity, stability, and selectivity.

In the preparation of nanomaterials, ILs and DESs play multiple roles as solvents, stabilizers, templating agents, and reaction media. As solvents, they can dissolve metal precursors and facilitate the synthesis of nanomaterials at low temperatures, which helps in fine-tuning of particle size and morphology. As stabilizers, they adsorb on the surface of nanoparticles to prevent aggregation and enhance dispersion. Certain ILs and DESs can also serve as templates to guide the formation of nanostructures with specific configurations like porous structures or nanotubes. Moreover, some ILs and DESs can act as both reaction media and catalysts or their precursors in chemical reactions, promoting the formation of nanomaterials. These characteristics demonstrate the significant application potential of ILs and DESs in synthesizing nanomaterials with specific shapes, sizes, and functions, which have indispensable roles in the field of catalysis.

Past studies have shown significant progress in using ILs and DESs to prepare high-performance cobalt-based catalysts through various techniques like electrodeposition, solvothermal technologies, and calcination. These catalysts have demonstrated exceptional capabilities in applications such as electrocatalytic water splitting. Despite these advancements, challenges such as low scalability, high cost, and environmental concerns persist in IL/DES-mediated cobalt catalyst research, signaling that further investigation is needed to address these issues:

The development of green synthesis technologies: As environmental awareness continues to grow, green synthesis technologies will become a focal point of future research. Therefore, developing more efficient and environmentally friendly IL/DES-mediated cobalt-based catalyst synthesis technologies will be an important direction for the future.

Optimization of catalyst performance: Although some high-performance cobalt-based catalysts have been reported, how to further improve their performance remains a challenging topic. Prospective research may focus on the design of catalysts, improvement of preparation processes, and the interaction between active components and carriers.

Development of multifunctional catalysts: To meet the increasingly complex demands of industrial production, the development of cobalt-based catalysts with multiple functions will become a trend in the future. For example, developing catalysts that can catalyze both water splitting and organic reactions.

In-depth study of catalytic mechanisms: Although there have been some studies on the catalytic mechanisms of IL/DES-mediated cobalt-based catalysts, many unknown questions still remain to be addressed. Future efforts could center on revealing the catalytic mechanisms of catalysts at the atomic level, providing theoretical guidance for the design and optimization of catalysts.

Expansion of practical applications: Currently, IL/DES-mediated cobalt-based catalysts have been applied in some areas, such as electrocatalytic water splitting. In the future, as research deepens and technology advances, these catalysts are expected to be applied in more fields, such as energy conversion (fuel cells, high-efficiency energy storage systems, etc.), environmental protection (pollutant degradation, waste gas treatment, etc.), and fine chemical engineering (synthesis of high-value-added chemicals, selective catalytic reactions, etc.).

Research of catalysts for extreme environments: With the extension of the hydrogen energy industry to complex application scenarios, the development of catalysts suitable for extreme environments has become urgent. For example, in acidic seawater electrolysis systems, chloride ion corrosion and complex electrolyte environments significantly reduce catalyst stability, making it critical to develop highly efficient chlorine-resistant hydrogen evolution/oxygen evolution catalysts. Recent studies have shown that phosphorus–tungsten dual-doped RuO_x nanocrystals [55] exhibit excellent corrosion resistance and catalytic activity in acidic seawater full decomposition, while constructing $CoP/MnP/Cu_3P$ heterojunctions [56] enables methanol oxidation-assisted seawater splitting, significantly enhancing catalyst adaptability across wide pH ranges. Additionally, by regulating the dd orbital coupling in PtPdCu medium-entropy alloy aerogels [57], pH-general methanol electro-oxidation catalysts have been developed, providing new insights for energy conversion in extreme environments. In the future, catalyst design for extreme conditions such as high salinity, strong acid/alkali, and high temperature requires further integration of atomic-scale structure regulation and interface engineering to enhance catalyst corrosion resistance and intrinsic activity.

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Conflict of interest: Authors state no conflict of interest.

Ethical approval: The conducted research is not related to either human or animal use.

Data availability statement: Data sharing is not applicable to this article as no datasets were generated or analyzed during the current study.

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