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Review

Progress in the Study of Transition Metal-Based Carbon Nanotube Composites for Electrochemical Hydrogen Evolution

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ABSTRACT: Hydrogen is an efficient, clean, and economical energy source, primarily due to its remarkably high energy density. Electrolytic water is considered an attractive and feasible method for hydrogen production. The high cost and scarcity of traditional Pt-based catalysts limit their large-scale application. Transition metals (TMs)-based composites, particularly those integrated with carbon nanotubes (CNTs), have emerged as promising alternatives due to their high conductivity, surface area, and ability to enhance the catalytic properties of TMs. Currently, there is no systematic summary of TMs-based CNTs composites for electrochemical hydrogen evolution reaction (HER). In this review, the main synthesis methods, including the wet chemical method, chemical vapor deposition, and electrochemical techniques, were first summarized. Then, the latest advancements of TMs/CNTs composites, focusing on their structure, electronic properties and superior HER catalytic performance, were systematically discussed. The catalytic mechanisms are meticulously examined, with particular emphasis on the pivotal role of CNTs in enhancing charge transfer and stabilizing metal nanoparticles. Finally, this review addresses the current challenges and future development directions for HER catalysts.

Keywords: Carbon nanotubes; Transition metals; Composites; Hydrogen evolution reaction

1. Introduction

Over recent decades, fossil fuels have been mined in large quantities in order to meet the rapidly growing global energy demand. However, this over-reliance on fossil fuels has caused serious negative impacts on the environment. To alleviate these problems, significant research efforts have been directed toward developing renewable energy systems that combine environmental safety, sustainability, and high efficiency [1–4]. Hydrogen is considered a highly promising clean fuel owing to its zero-emission combustion and environmentally benign byproduct (water), positioning it as a sustainable alternative to fossil fuels [5–7]. Electrocatalytic water splitting under acidic or alkaline conditions represents one of the most viable pathways for sustainable hydrogen generation among current production technologies [8–10]. The theoretical voltage required for water electrolysis is 1.23 V, significantly lower than the operational voltages (1.8–2.0 V) employed in commercial electrolyzes [11]. Consequently, the development of highly efficient catalysts capable of delivering low overpotential (η) is essential for optimizing the energy efficiency of water electrolysis [12]. Currently, Pt is considered benchmark HER electrocatalysts owing to their exceptional catalytic activity and near-zero Gibbs free energy (ΔG_{H^*}) across a broad pH range. Despite their superior performance, platinum catalysts face critical barriers to industrial adoption due to supply constraints, economic impracticality, and stability concerns under prolonged operation [13–15]. Therefore, researchers have been committed to finding electrocatalysts with abundant resources, high efficiency, high activity, stability and sustainability.

Non-precious transition metals (TMs) have become a research hotspot in the field of hydrogen evolution catalysts due to their abundant reserves, relatively low cost, and ease of design and modification. However, their catalytic activity still lags significantly behind that of precious metals [16–18]. Despite their promise, TMs catalysts still face significant limitations, particularly their tendency to aggregate on electrode surfaces. This aggregation behavior obstructs

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interfacial charge transfer and reduces the electrochemically active surface area (ECSA), ultimately compromising their hydrogen evolution performance [19]. Consequently, the restricted surface reaction kinetics and impaired charge carrier mobility in TMs catalysts collectively lead to suboptimal HER performance. To overcome these limitations, engineering charge-transfer pathways between TMs and electrodes emerges as an effective strategy to accelerate the sluggish carrier migration kinetics during HER. As prototypical 1D carbon materials, carbon nanotubes (CNTs) combine with electrochemically active TMs to construct high-performance HER catalysts with enhanced activity and stability. Meng et al. [20] fabricated a CNT/C/$Ru_{0.37wt\%}$-700 catalyst that prevents the stacking of Ru nanoparticles on CNT, demonstrating outstanding catalytic performance. The elemental mapping confirms the uniform distribution of Ru on CNT surfaces (Figure 1a), demonstrating CNTs' capability to disperse TMs. CNTs, as conductive scaffolds with distinctive hollow architectures, exhibit exceptional electrical conductivity, extensive surface area, and remarkable corrosion resistance [21–23]. Liang et al. [24] employed a simple method to load Pt onto CNTs grafted with carbon quantum dots (CQDs). This catalyst exhibited remarkable stability in the HER within acidic solutions. Many Pt atomic clusters on CQDs (5 nm) are found in 1% Pt/CQDs/CNT from Figure 1b. When employed as protective coatings for TMs, CNTs have demonstrated remarkable effectiveness in boosting catalytic performance while ensuring long-term durability [25–27].

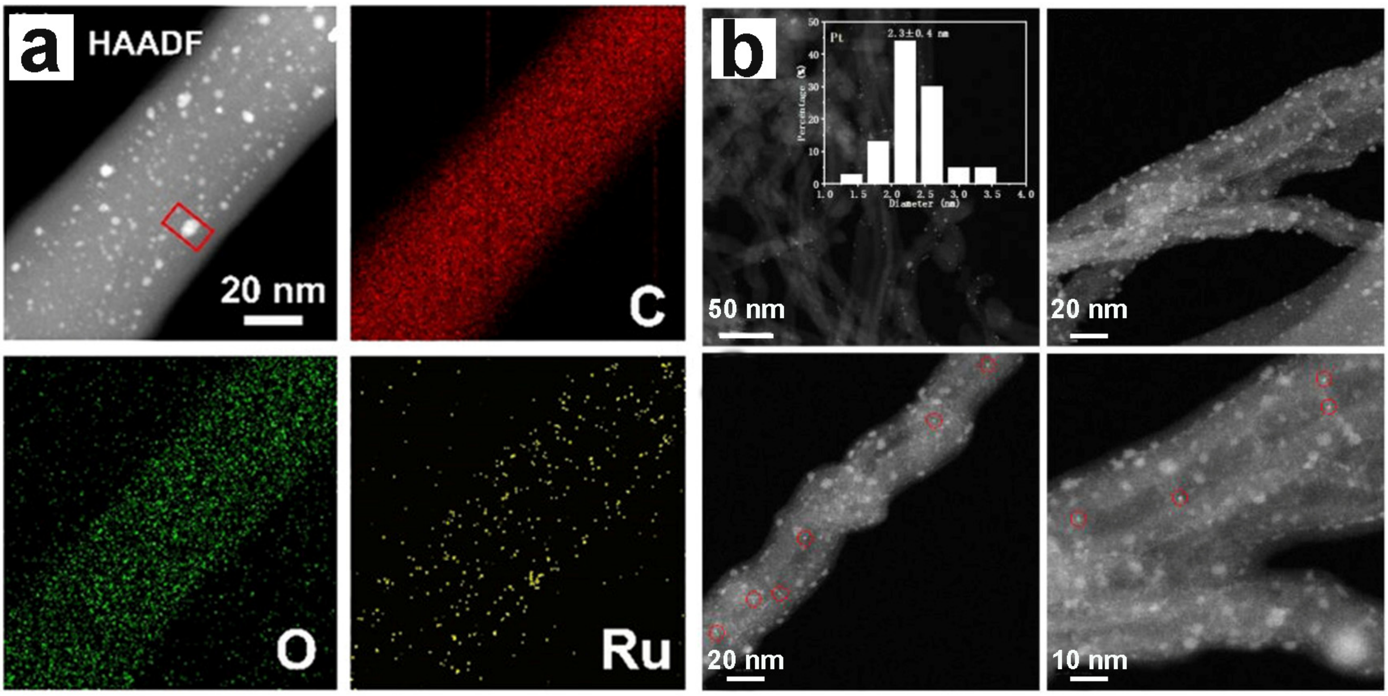

Figure 1. (**a**) TEM-EDS image of CNT/C/$Ru_{0.37wt\%}$-700 updated from reference [20]. 2023, WILEY. (**b**) HAADF-STEM image of 1%Pt/CQDs/CNT updated from reference [24]. 2021, WILEY.

In the past five years, TMs and CNTs have garnered increasing attention in the field of electrocatalytic HER. These materials are highly regarded not only for their abundant reserves and relatively low cost but also for their significant flexibility in design and modification. Unbeom et al. [28] developed a machine learning-guided strategy combining Bayesian genetic algorithm (BGA) predictions with experimental/theoretical validation to optimize Ni@CQD HER electrocatalysts. Among six transition metals (Ni, Co, Fe, Mn, Zn, and Ag), Ni was identified as the optimal dopant. The optimized catalyst exhibited exceptional performance with an overpotential of only 151 mV at 10 mA cm^{-2} under the determined ideal reaction conditions. Yi et al. [29] synthesized Pt/CNT45 catalysts with only 1 wt% Pt loading via a room-temperature, H_2-free discharge-driven reduction (RT-DR) process. For HER electrocatalysis in acidic, neutral, and alkaline electrolytes, Pt/CNT45 exhibited superior activity compared to commercial Pt/C benchmarks. This study pioneers a new strategy for developing low-Pt-content catalysts with broad-pH HER efficiency, offering significant potential for industrial applications. Zhang et al. [30] systematically summarized the latest advancements in multi-interface engineering of nickel-based electrocatalysts to enhance their catalytic activity for alkaline HER. Su et al. [31] summarized the existing defect engineering strategies, revealing the distinct properties of various defect-rich transition metal dichalcogenide (TMD) catalysts, which provided valuable insights for designing high-performance TMD electrocatalysts. However, to the best of our knowledge, a comprehensive review of TMs-based CNT composites as catalysts for HER has not yet been conducted. A thorough and systematic evaluation of the underlying mechanisms, modification methodologies, and structure-activity correlations in TMs-CNT composite HER electrocatalysts is of critical importance.

In this review, the development history and preparation methods (e.g., wet chemical method, electrochemical deposition and chemical vapor deposition method) of TMs-based CNTs composite electrocatalysts are summarized (Section 2). Furthermore, the study provides an in-depth discussion on how transition metals (e.g., Pt, Ru, Fe, Co, Ni, and their polymetallic alloys) influence both the morphology of carbon nanotube catalysts and their HER performance (Section 3). The new role of TMs-based CNTs composite in electrocatalytic hydrogen evolution was also mentioned. Finally, the main challenges and opportunities are summarized and prospected (Section 4).

2. Synthesis Method of TMs/CNTs Composite Catalysts

CNTs possess a high specific surface area, excellent electrical conductivity, and superior mechanical strength, making them widely explored as electrode materials in electrochemical applications [32,33]. To enhance the performance of CNTs-based catalysts, researchers have developed CNTs composites by integrating CNTs with TMs. The synthesis methods of TMs/CNTs composite catalysts mainly include three types: wet chemical method [34], electrochemical deposition [35], and chemical vapor deposition (CVD) method [36]. The wet chemical method uses small amounts and has high utilization, this point is very important for noble metal catalysts, can prepare relatively small-sized particles, but the particle sizes are not uniform. Differently, the electrochemical deposition method can precisely control the content and morphology of deposited materials by adjusting experimental parameters. These two methods generally load TMs on the outer walls of CNTs, and usually face the problem of catalyst corrosion by acids and alkalis. However, CVD method enables scalable catalyst fabrication, while the encapsulation of TMs inside CNTs ensures exceptional catalytic stability over extended periods. This section discusses the research progress on synthesis methods of TMs/CNTs composite catalysts.

2.1. Wet Chemical Method

Wet chemical method has many advantages in modifying CNTs such as simple, low temperature and low pressure, which makes the reaction conditions relatively mild and controllable [37]. Typically, the catalyst is prepared by bringing a support into contact with an aqueous solution of metal salts, allowing the solution to be adsorbed or stored within the capillaries of the support. The excess solution is then removed, followed by drying, calcination, and activation. Meanwhile, high-purity materials can be synthesized using wet chemical method.

For examples, Rapakousiou et al. [38] prepared an efficient electrocatalyst combining CNTs and Pt nanoparticles (NPs) by wet chemical method (Figure 2a). This electrocatalyst achieved a η of 77 mV at 10 mA cm^{-2}, attributed to the high surface area and superior conductivity of CNTs. Wang et al. [39] used a simple wet chemical method to modify CNTs with ultrafine PtNPs. The prepared Pt/CNTs electrocatalyst exhibited excellent HER performance in 0.5 M H_2SO_4 solution, with a low η of 24 mV at 10 mA cm^{-2}. The enhanced catalytic performance originates from the excellent electrical conductivity of CNTs coupled with the synergistic contribution of abundant active sites furnished by ultrafine Pt NPs. Similarly, Pagliaro et al. [40] synthesized a Ni/CNT-3^{Ni} through a straightforward wet chemical method. This research presents a method for preparing Ni NPs anchored on N-functionalized CNTs with tunable nitrogen content and alkaline surface characteristics (Figure 2b). The unique hierarchical structure of the Ni/CNT-3^{Ni} composite, along with the interaction between Ni NPs and CNTs, endows it with excellent electronic conductivity and abundant active sites. Consequently, this composite exhibits significantly enhanced electrocatalytic HER activity and stability, exhibited an HER Tafel slope (66 mV dec^{-1}) approaching that of benchmark Pt electrocatalysts.

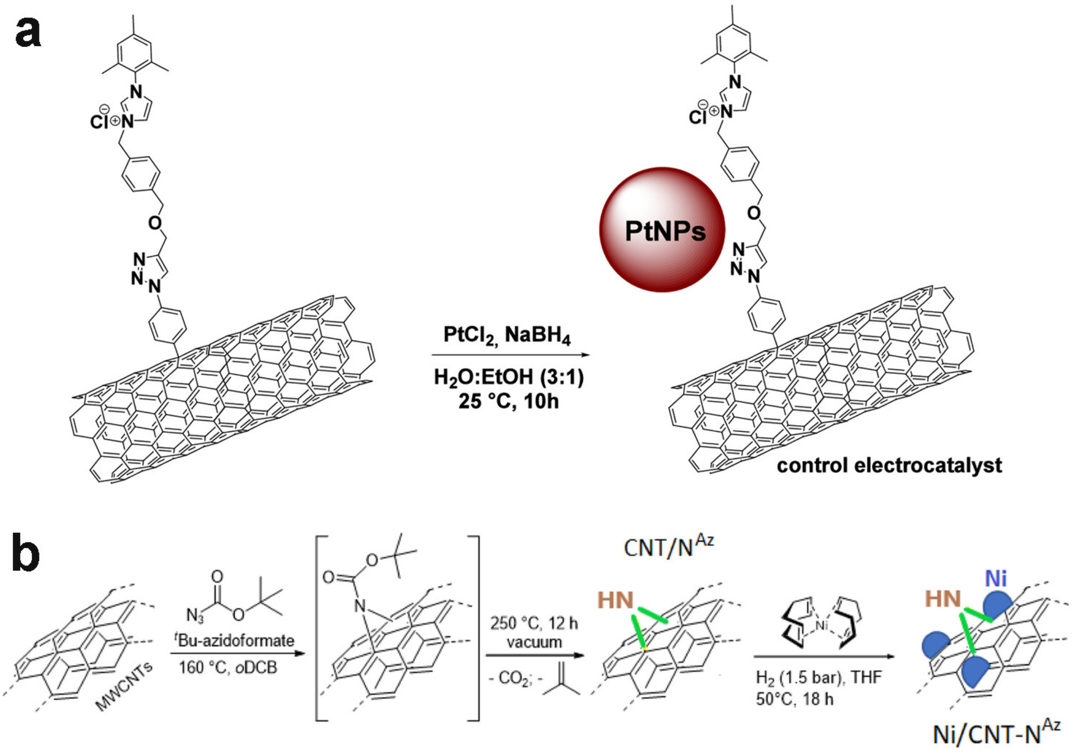

Figure 2. (**a**) Preparation of MWCNTs-NHC-PtNPs Electrocatalyst updated from reference [38]. 2025, ACS. (**b**) Preparation of Ni/CNT-N^{Az} (3^{Ni}) Electrocatalyst updated from reference [40]. 2021, ACS.

2.2. Electrochemical Deposition

Conventional binders are known to adversely affect electrode conductivity, resulting in impaired electrocatalytic activity for water decomposition reactions [41–43]. Furthermore, detachment of active materials from current collectors may occur, thereby deteriorating electrode stability. Electrodeposition is an electrochemical process used to deposit metals or alloys onto the surface of a conductive substrate. The fundamental principle involves applying an external current to reduce metal ions at the electrode surface, thereby forming a metallic film or coating. Figure 3 shows the representative electroplating cell. Electrodeposition experiment can directly grow active materials on the substrate, which perfectly overcomes the above shortcomings. This method has the following advantages: firstly, electrodeposition technology is a simple and low-cost mass production method. Secondly, in the electrodeposition experiment, many experimental parameters can be modulated. For example, the deposited material's content and morphology can be precisely controlled through charge quantity manipulation and deposition technique optimization, respectively [44]. In addition, electrochemical growth makes close contact between TMs and CNTs, thus promoting electron transfer between them. Therefore, the composite material fabricated via this approach possesses abundant active sites and enhanced conductivity, demonstrating superior catalytic performance.

Chen et al. [35] successfully prepared a CNT@NiSe/SS HER catalyst by electrodepositing NiSe NPs onto CNTs. The synthesized composite nanotubes formed a densely packed, interconnected porous network on the SS substrate. Consequently, the CNTs framework facilitates the controlled growth of nanostructured NiSe. This structure results in a large ECSA, thereby exhibiting excellent HER performance. Similarly, Zhao et al. [45] integrated CNTs with Ni-$Ni(OH)_2$ heterostructures through composite deposition followed by *in situ* oxidation, fabricating a self-supporting 3D CNTs-Ni-$Ni(OH)_2$ catalyst for HER applications. CNTs have large specific surface area, which can support active materials, facilitate the formation of three-dimensional structures, and quickly transfer participating electrons in the catalytic process [46]. CNTs and spherical Ni particles formed abundant wrinkled boundary structures, supplying sufficient catalytic area. Numerous studies demonstrate that the exposed two-dimensional edges serve as critical active sites in catalytic reactions [47–49]. Notably, the as-designed CNTs-Ni-$Ni(OH)_2$ electrode exhibits both enhanced operational durability and reduced η relative to benchmark Pt/C catalysts under electrochemical testing. The outstanding catalytic performance arises from the cooperative interplay between CNTs doping effects, heterostructure interfaces, and electrodeposition-enabled structural integrity. Despite these advantages, electrodeposition necessitates specialized equipment and trained personnel to prevent non-uniform deposition and impurity co-deposition.

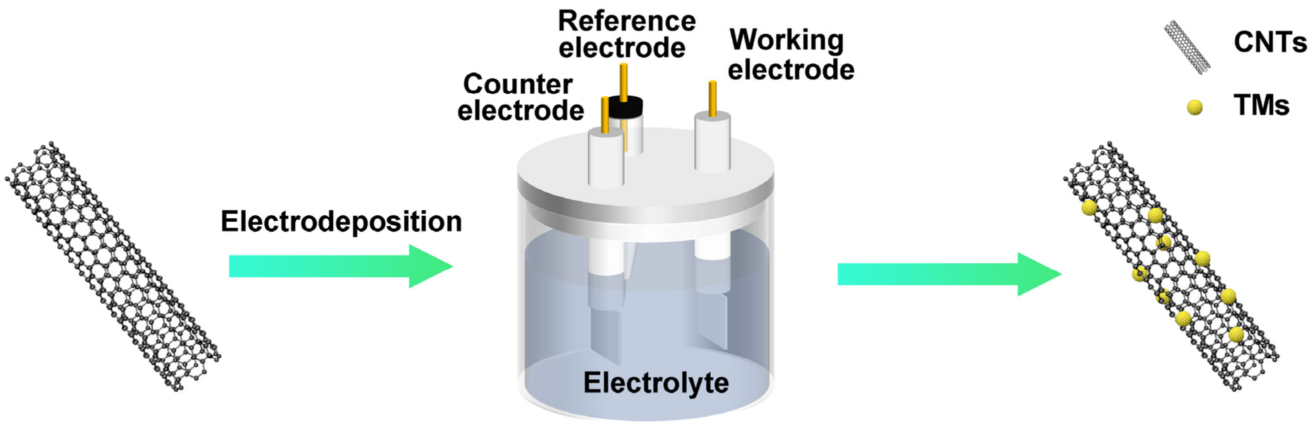

Figure 3. Representative electroplating cell.

2.3. Chemical Vapor Deposition Method

Currently, TMs have emerged as extensively investigated electrocatalytic materials for the HER due to their promising catalytic potential. Unlike Pt group metals (PGMs), TMs are typically deposited on current collectors such as foamed nickel [50], carbon fiber cloth [51] and titanium plate [52]. Previous studies have demonstrated that direct growth of Ni_2P or M-Ni_2P on carbon cloth (CC) simultaneously enhances HER activity and enables scalable catalyst production [53]. However, CC-supported TMs catalysts still encounter inherent limitations, including inadequate conductivity and metal aggregation, which hinder interfacial charge transfer and result in insufficient ECSA for hydrogen evolution. Therefore, the TMs/CC system exhibits constrained surface reaction kinetics and impaired charge carrier mobility, collectively leading to suboptimal HER performance. The combination of TMs and CNTs perfectly solves this problem. At present, the common methods for preparing CNTs are arc discharge (AD) [54], laser ablation (LA) [55] and chemical vapor deposition (CVD) [56]. CVD generally requires TMs as catalysts to catalyze the growth of CNTs. By this method, TMs and CNTs can be perfectly combined. At the same time, chemical vapor deposition, especially catalytic chemical vapor deposition (CCVD) [57] provides an attractive method for the combination of CNTs with TMs because of its unique characteristics, low cost and controllable production of CNTs. The CCVD method can directly produce high-purity carbon nanotube arrays on substrates. The growth of CNTs is selective, typically favoring surfaces of TMs such as Fe, Co, and Ni. Additionally, CCVD can achieve high-yield growth of CNTs at relatively low temperatures, which is highly advantageous for large-scale production [58]. 3d TMs coupled with carbon composites, especially TMs encapsulated with CNTs (TMs@CNTs), has been proved to be a competitive HER catalyst. Within this composite, CNTs integrate three critical functions: corrosion resistance for TMs in harsh media, spatial nanoconfinement to facilitate interfacial charge transfer, and HER-active site generation through TM-mediated electron density modification. Cao et al. [59] synthesized a Co_4N@CoSA/-CNT/CC catalyst for electrochemical hydrogen evolution (Figure 4a). The current density of Co_4N@CoSA/N-CNT/CC is 10 mA cm^{-2}, and the η is 89 mV (Figure 4b,c). The time current response test (*i*-*t* test) of Co_4N@CoSA/N-CNT/CC was carried out for 50 hours at an overvoltage of 86 mV (Figure 4d). This is mainly because the CNTs grown by vapor deposition method wrap Co in the skeleton, which reduces the corrosion of electrolyte to the catalyst.

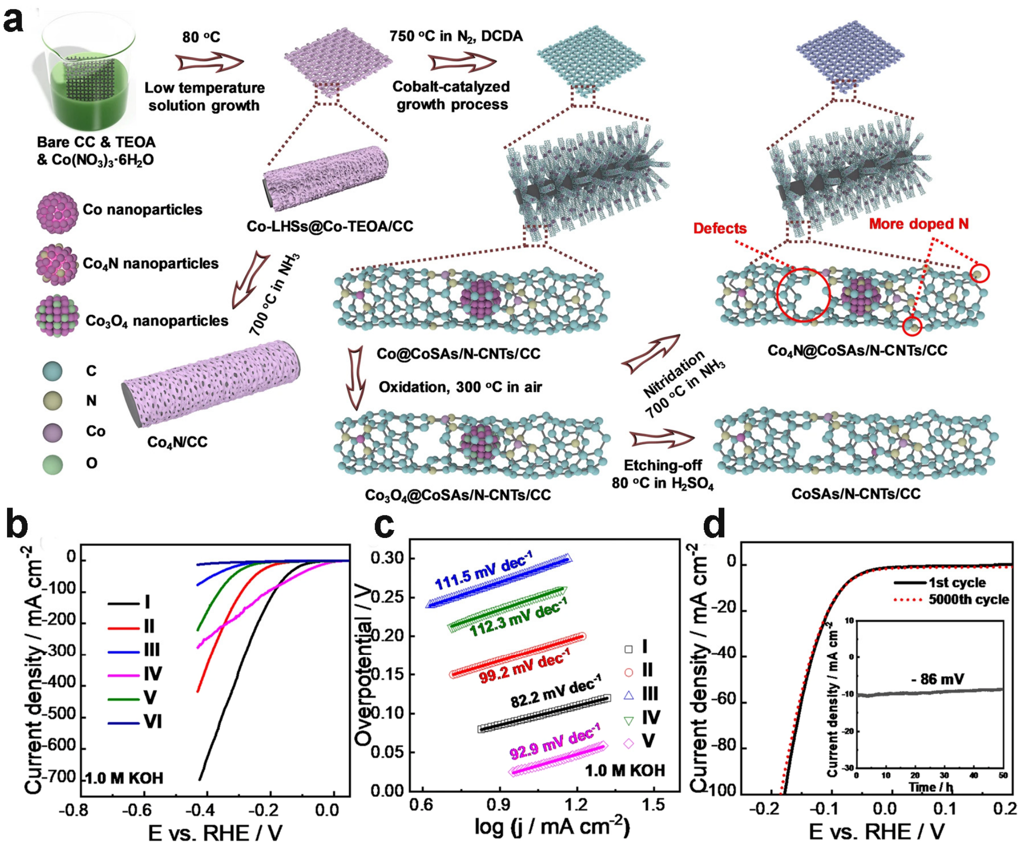

Figure 4. (**a**) Schematic illustration showing the fabrication process of Co_4N@CoSA/N-CNT/CC. (**b**) LSV curves and (**c**) Tafel slopes of (I) Co_4N@CoSA/N-CNT/CC, (II) Co@CoSA/N-CNT/CC, (III) CoSA/N-CNT/CC, (IV) 20 wt% Pt/C, (V) Co_4N/CC, and (VI) bare CC. (**d**) Stability tests updated from reference [59]. 2021, Springer Nature.

3. Research Progress of TMs/CNTs Composite Catalysts in HER

TMs refer to a series of metallic elements in the *d* region of the periodic table, including precious metals (Au, Ag, Pt, Rh, Ir, Ru and Os) and common metals such as manganese, Fe, Co, Ni, Cu and Zn. Due to their partially filled d orbitals, TMs frequently possess unpaired electrons, enabling facile complexation with various metallic or nonmetallic elements to attain electronic stability. The quantum size effect and small size effect of nanomaterials can significantly improve the electrical and magnetic properties of TMs-based nanomaterials. TMs-based nanomaterials include TMs elemental nanomaterials and TMs sulfides [60–62], TMs selenides [63–65], TMs phosphide [66–68], TMs borides [69,70] *etc.* Because of its unique physical, optical properties and electronic structure, TMs-based nanomaterials have emerged as promising alternatives to Pt-group materials for HER applications. The hybrid composite material of TMs and CNT can not only effectively improve conductivity, but also optimize its activity through synergistic effects, solving the problem of corrosion of metal active sites in electrocatalytic processes, thereby improving the stability of hybrid composite catalysts [71,72].

3.1. Noble Metal/CNTs Composite Catalysts

In light of the limited literature on experimental studies concerning Pd, Ir, and Os carbon nanotube composite catalysts, this section will focus exclusively on Pt and Ru. The analysis of the remaining metals will be systematically addressed in Section 3.3.

3.1.1. Pt /CNTs Composite Catalysts

Substantial efforts have been devoted to developing advanced catalysts for η reduction and HER efficiency enhancement. To date, Pt-based nanomaterials are recognized as the most effective electrocatalysts for HER, primarily due to their low absolute value of ΔG_{H*} (−0.09 eV), which is close to zero [63]. Pt exhibits both high electrocatalytic activity and exceptional stability, establishing it as the benchmark for commercial electrocatalysts [73,74]. Usually, in the electrocatalytic electrolytic reaction, an electrocatalyst is coated on the electrode surface to reduce the η and accelerate the kinetic reaction [75]. However, the scarcity of Pt in nature and its inadequate long-term stability under operational conditions hinder large-scale production, thereby limiting the widespread adoption of hydrogen technologies [76]. Therefore, it is crucial to minimize the Pt content in electrocatalysts while maintaining high catalytic activity.

Zhang et al. [77] dispersed Pt NPs on multi-walled Ni (Pt/CNT-H) as an effective electrocatalyst for HER. The catalyst demonstrated outstanding electrocatalytic activity in acidic media. At a current density of 10 mA cm^{-2}, the η of Pt/CNT-H was 19 mV, significantly lower than the η of the Pt/C catalyst (38 mV). The enhanced HER activity of Pt/CNT-H arises from the combined effects of Pt-Ni electronic synergy and a cross-linked 3D conductive network. Tavakkoli et al. [78] introduced a novel electrochemical method for effectively dispersing Pt atoms on the side walls of single-walled CNTs. DFT calculation shows that the SWNT sidewall can effectively fix Pt atoms. The findings highlight SWNTs' promise as substrate materials for single-atom Pt catalyst stabilization. Theoretical calculations further confirm that single-atom Pt sites anchored on SWNTs exhibit HER electrocatalytic activity comparable to conventional bulk Pt catalysts. The present work pioneers an innovative strategy for developing electrochemically active catalysts containing minimal Pt loading. The application of CNTs allows for the drastic reduction of precious metal usage, a critical advantage for scalable commercialization.

To date, Pt maintains its status as the most effective HER catalyst, demonstrating optimal balance between reaction kinetics, durability, and practical applicability. This makes it suitable for industrial applications, such as proton exchange membrane (PEM) electrolyzers in acidic environments [79,80]. Nevertheless, the acidic operational environment in PEM electrolyzers induces significant cathode degradation. On the traditional carbon black substrate, Pt nanoclusters are easy to aggregate during the on/off electrochemical cycle of electrolytic cell connected with renewable energy. So far, this has led to the confrontation between ultra-low Pt load (<1000 ng Pt cm^{-2}) and the high durability requirements of PEM electrolyzers. Rajala et al. [81] established a facile and scalable approach to fabricate Pt nanowires (PtNWs) on single-walled CNTs (SWCNTs) (Figure 5a), effectively reducing the reliance on platinum group metals. The Pt/SWNT-O_3 catalyst incorporates high aspect ratio PtNWs onto single-SWNTs with an ultra-low Pt content (340 ng_{Pt} cm^{-2}) (Figure 5c) for the HER. In acidic aqueous solutions, its activity (10 mA cm^{-2} at −18 mV *vs.* RHE) is comparable to that of state-of-the-art Pt/C (Figure 5b) and it also exhibits excellent stability (Figure 5d). Tang et al. [82] achieved ultralow overpotential water splitting capability in alkaline solutions by incorporating platinum nanoparticles bonded to carbon nanotubes (Pt-NPs-bonded@CNT) with strong Pt-C bonds (Figure 5e). the Pt-NPs-bonded@CNT also had outstanding hydrogen evolution performance in 1.0 M KOH, as presented in Figure 5f. This enhancement arises from the synergy between PtNWs and SWNTs-PtNW edge sites simultaneously facilitate hydrogen adsorption and reduce H-H repulsion, leading to superior HER activity.

Pt-based materials remain the performance benchmark for hydrogen evolution catalysis in acidic media [83,84]. However, Pt-based catalysts exhibit significantly restricted HER activity in alkaline media. Researchers have fabricated diverse Pt-derived HER electrocatalysts using varied design approaches [85–88]. Support materials optimize Pt-based HER catalysts by both anchoring ultrafine NPs and facilitating interfacial electronic interactions between Pt and the substrate [87]. Modulating the chemical state of Pt represents an effective strategy to enhance catalytic performance through electronic structure optimization [86]. It is widely reported in the literature that the active site of HER in Pt-based catalysts is metal Pt [86,88]. However, by changing the chemical state of Pt, some recent reports show that the high valence state of Pt with Pt-O bond (such as PtII) may actually be the real catalytic center, which shows better HER performance than metal Pt [89,90]. Engineering Pt-based catalysts with high-valence Pt centers and optimized support materials could enable efficient alkaline HER. In summary, HER electrocatalyst was prepared by transforming Pt metal into platinum compounds (such as oxides, tellurides and alloys), which had good electrocatalytic activity and stability in both alkaline and acidic electrolytes [91–94]. These materials can be combined with CNTs, which will provide more choices for industrial HER electrocatalyst.

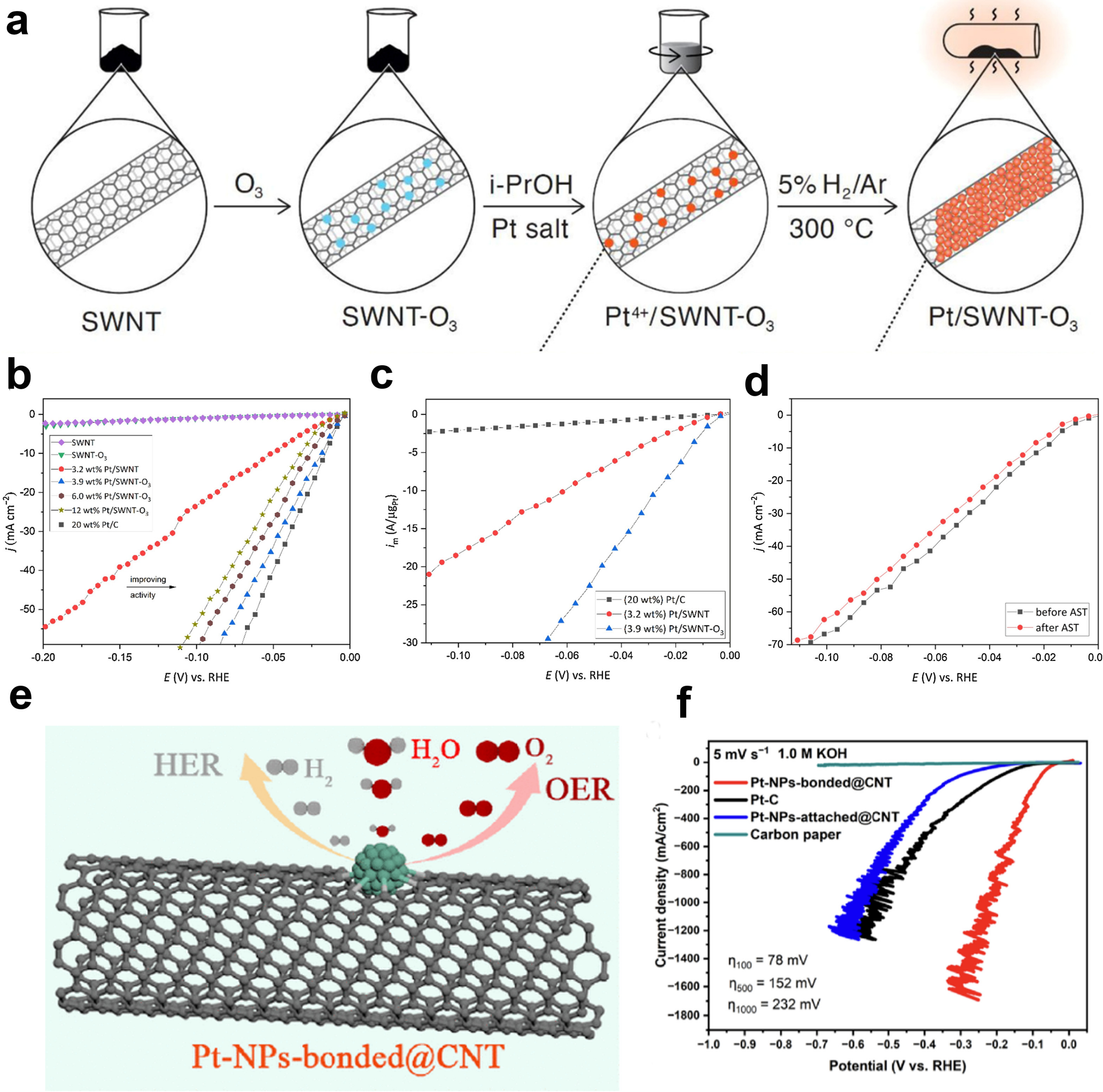

Figure 5. (**a**) Schematic illustration of the synthesis of Pt/SWNT-O_3 HER polarization curves for Pt/SWNT catalysts (**b**) electrode area (**c**) Pt mass. (**d**) HER polarization curves for Pt/SWNT-O_3 before and after an accelerated stress test (AST) updated from reference [81]. 2020, Elesvier. (**e**) Schematic illustration of Pt-NPs-bonded@CNT toward bifunctional catalytic HER and oxygen evolution reaction (OER). (**f**) HER LSV curves of Pt-NPs-bonded@CNT, Pt-NPs-attached@CNT, Pt-C, and carbon paper in 1.0 M KOH updated from reference [82]. 2024, ACS.

3.1.2. Ru/CNTs Composite Catalysts

Pt exhibits optimal hydrogen adsorption energy, minimal η, superior exchange current density and favorable Tafel slope characteristics, establishing it as the benchmark HER electrocatalyst [95]. Beyond the prohibitive cost and limited availability, Pt exhibits unsatisfactory electrochemical stability due to dissolution in corrosive electrolytes and irreversible nanoparticle aggregation through Ostwald ripening mechanisms [96,97]. With its competitive price (one-third of Pt), operational durability, and high hydrogen evolution efficiency, Ru is extensively employed in metallic catalyst systems [98,99]. Despite numerous studies on Ru-based electrocatalysts, few demonstrate Pt-comparable HER activity. However, compared with Pt NPs, Ru NPS shows greater binding energy which makes it easy to reunite under turnover conditions [100]. Consequently, anchoring and dispersing catalytic sites on conductive supports is a vital strategy for developing durable electrocatalysts. This approach not only prevents metal aggregation but also enhances electron transfer between the catalyst and the electrode [101]. The unique combination of CNTs' large surface area, metal-comparable conductivity, robust stability, and moderate hydrophilicity enables efficient electrocatalytic applications in aqueous environments [102].

Recent studies have demonstrated that CNTs effectively stabilize Ru NPs on HER mixed electrode. Liu et al. [103] developed a novel Ru catalyst (Ru@CNT) supported on nitrogen-doped CNTs, which exhibited excellent catalytic performance in 1 M KOH. A current density of 10 mA cm^{-2} can be achieved with a η of 36.69 mV, and its Tafel slope is 28.82 mV dec^{-1}. The exceptional catalytic performance primarily originates from atomically dispersed Ru species stabilized through chelation on N-doped CNTs substrates. The 1D porous architecture of N-CNTs further enhances active site accessibility by providing abundant anchoring opportunities. Wang et al. [104] oxidized commercial CNTs with nitric acid to introduce oxygen-containing functional groups, particularly carboxylic –COOH, onto their surfaces, resulting in oxidized carbon nanotubes (OCNTs) Ruthenium nanoparticle catalysts were prepared on the support of (Ru@OCNT). Due to its excellent HER performance, Ru@OCNT electrocatalyst has wide applicability in large-scale hydrogen production. Romero et al. [105] combined the versatility of organic synthesis methods for metal-based nanostructures with thermal oxidation treatments to create Ru-containing nanomaterials supported on CNTs. This strategy allows a series of hybrid nanomaterials with different Ru/RuO_2 compositions and different structural sequences to be obtained. The electrode of NPs containing RuO_2 core and surface metal Ru is better than that containing pure RuO_2 NPs or Ru NPs. The initial η of Ru@RuO_2/CNT/GC electrode is 200 mV, and the current density is 10 mA cm^{-2} when the η is 272 mV. The calculation results show that this is due to two factors: (1) The amorphization of external Ru atoms increases the number of hydrogen atoms that can be adsorbed; (2) The Ru center on the surface is partially oxidized by RuO_2, which overall weakens the adsorption of H.

Meng et al. [20] proposed a coaxial wrapping method of defective amorphous CNTs sponge network loaded with Ru NPs. The presence of amorphous carbon facilitates both uniform dispersion and size confinement of Ru NPs. The incorporation of oxygen vacancies enables electronic structure modulation of metal sites, enhancing charge transfer kinetics and consequently boosting catalytic efficiency. To elucidate the underlying catalytic mechanism, a theoretical model was developed (Figure 6a). The defect-induced electron transfer in Ru effectively downshifts its d-band center, thereby optimizing the adsorption energy of water molecules and significantly promoting their dissociation and subsequent dehydrogenation in the HER. Three typical hydrogen adsorption sites were selected (Figure 6b), with site 3 representing the equatorial region. The ΔG_{H^*} value is closer to 0 eV (Figure 6c), indicating higher catalytic efficiency. In summary, computational results demonstrate that amorphous carbon-to-Ru charge transfer modulates Ru-H binding energy to thermodynamically optimal levels, thereby maximizing HER catalytic efficiency.

Electrocatalysts with Ru NPs anchored on multi-walled carbon nanotubes (Ru@MWCNT) can catalyze HER with excellent activity. Uniform and small Ru NPs can be formed by introducing carboxylic acid groups (–COOH) into MWCNT to form Ru carboxylic acid complexes. Kweon et al. [106] reported that Ru NPs are uniformly deposited on MWCNTs as an efficient HER catalyst. HER efficiency of Ru@MWCNT and Pt/C catalyst was evaluated in 1.0 M KOH solution (Figure 6d). The smaller the slope of Tafel, the faster the catalytic reaction of Ru@MWCNT is than that of Pt/C (Figure 6e). Ru@MWCNT exhibits a superior exchange current density (2.4 mA cm^{-2}) compared to Pt/C (1.4 mA cm^{-2}), demonstrating enhanced HER activity in alkaline electrolytes (Figure 6f). The catalyst's superior HER activity stems from its enlarged ECSA and improved charge transport properties [107–109]. However, CNTs' strong hydrophobic character often causes metal NP coalescence into oversized particles with insufficient Ru-CNT interfacial interactions [110,111]. Heteroatom doping (S/N/O) enhances CNTs hydrophilicity, improving noble metal-CNT affinity and facilitating interfacial electron transfer. Lin et al. [112] demonstrated effective structural coupling between ruthenium nanoclusters and phosphorus- and oxygen–doped CNTs (Ru-POCA). The performance comparison of HER electrocatalyst of noble metal–based carbon nanotube composites is shown in Table 1.

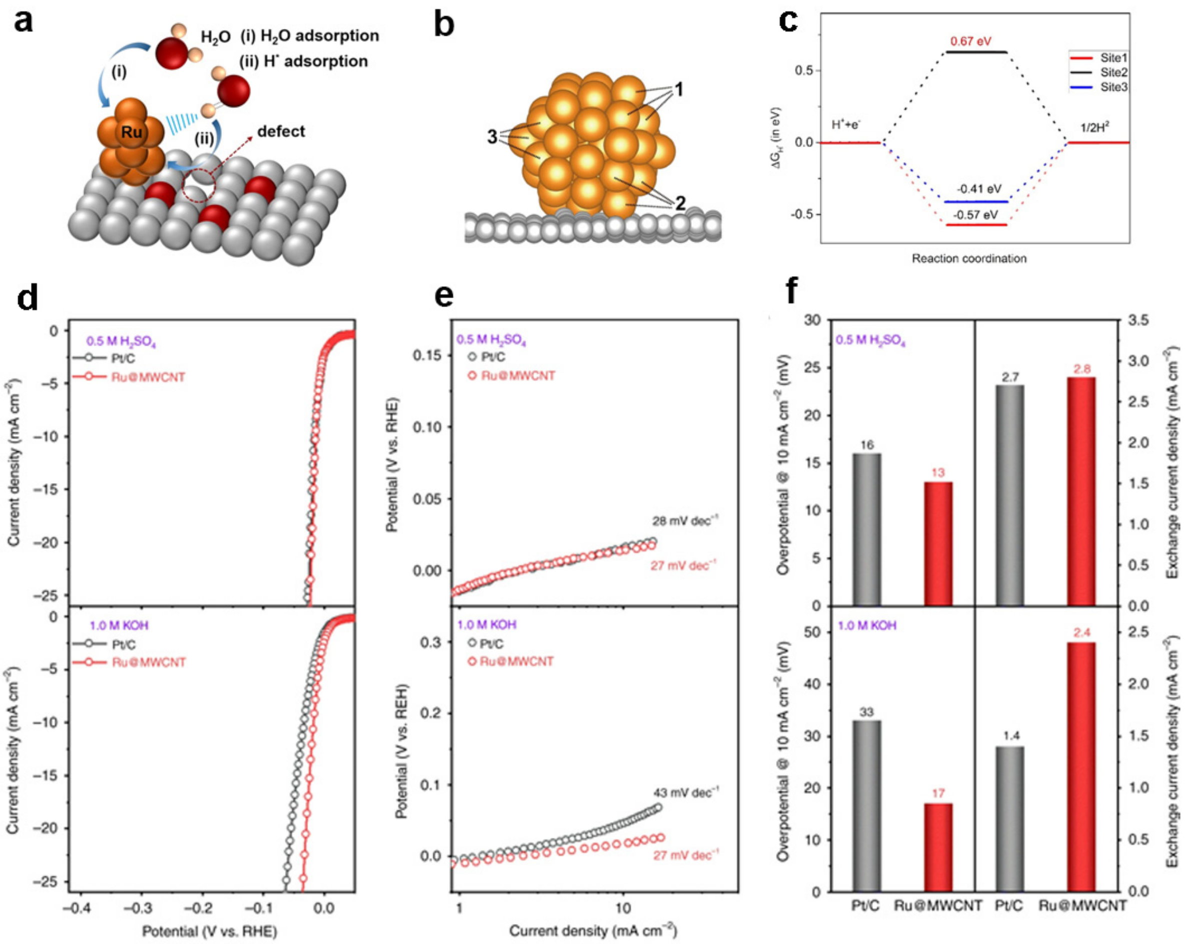

Figure 6. (**a**) Reaction mechanism and theoretical calculation and (**b**) mechanism diagram of electrocatalytic hydrogen evolution of catalyst CNT/C/$Ru_{0.37}$. (**c**) The ΔG_{H^*} and projected density of states updated from reference [20]. 2023, WILEY. (**d**) LSV of HER. (**e**) Tafel plots. (**f**) exchange current density updated from reference [106]. Springer Nature.

Table 1. Noble metal/CNTs composite catalysts for HER.

Material	η_{10}/mV	Tafel Slope (mV·dec^{-1})	Stability	Electrolyte	Reference
Pt-NPs-bonded@CNT	78 (η_{100})	28.6	125 h	1.0 M KOH	[82]
Pt/SWNT-O_3	18	——	2000 h	0.5 M H_2SO_4	[81]
400-SWNT/Pt	27	38	5000 cycles	0.5 M H_2SO_4	[78]
Pt/CNT-H	19	60.3	1000 cycles	0.5 M H_2SO_4	[77]
c-CNT-0.68@TpBpy-Ru	112	160	12 h	1.0 M KOH	[113]
Ru@OCNT	13.2	45.4	10 h	1.0 M KOH	[104]
Ru@CNT	36.68	28.82	10 h	1.0 M KOH	[103]
Ru@MWCNT	17	27	10,000 cycles	1.0 M KOH	[106]
Ru@MWCNT	13	27	10,000 cycles	0.5 M H_2SO_4	[106]
CNT/C/$Ru_{0.37wt\%}$-700	36.2/38.3	127/80	5000 cycles	0.5 M H_2SO_4/1.0 M KOH	[20]
r-RuO_2-10'/CNT-/GC	115	77	——	1 M H_2SO_4	[105]
Pt@MC-VA	208 (η_{500})	28	24 h	0.5 M H_2SO_4	[114]
Ru-POCA	40/22	27.1/28	15 h	0.5 M H_2SO_4/1.0 M KOH	[112]
Pt/CNTs	24	29	——	0.5 M H_2SO_4	[39]

3.2. Non-Noble Metal/CNTs Composite Catalysts

Some TMs (Ni, Co, W, Mo, Fe, *etc.*) can provide adsorption/desorption sites for reaction intermediates, change the adsorption/desorption ability of adjacent metal atoms H, and promote the electrocatalytic process. The catalytic performance of non-noble metals follow the following order: Ni > Co > Fe, Co > W > Cu > V > Zr [115]. For sustainable energy applications, catalysts composed of earth–abundant, low-cost elements are crucial to ensure economic feasibility. This chapter only focuses on the electrochemical hydrogen evolution catalysts made of Fe, Co and Ni [116].

3.2.1. Fe/CNTs Composite Catalysts

Fe is abundant in soil and possesses good electrical conductivity, showing great potential for electrocatalytic hydrogen evolution across the entire pH range [117]. However, in aqueous environments, especially under acidic conditions, iron is prone to corrosion, leading to material and performance degradation. These shortcomings urge researchers to look for cheap, available and stable support materials to achieve efficient catalytic reduction of protons to produce hydrogen. Jin et al. [118] prepared and characterized three new iron phosphine complexes FeP^R (R = F, H, Me) and their covalently bonded CNT hybrids CNT-F-FeP^R. Therefore, it may be a feasible strategy to covalently connect CNTs with catalytic metal complexes such as FeP^R (R is defined as ligand substituent) to improve the HER performance in aqueous medium. CNT-f-FeP^F exhibits superior electrochemical performance in aqueous media.

TMs oxides are good candidates as electrocatalysts in HER reaction [119]. Shi et al. [120] successfully synthesized a new type of Fe_3O_4 NPs by a simple method, and wrapped it in a dendritic carbon layer (DCL) structure wrapped with hollow carbon nanotubes (HCNTs). The composite material demonstrated superior HER catalytic activity owing to the synergistic interplay between N dopants, metal oxide NPs, and hollow CNTs architectures. This distinctive architectural configuration provides novel insights for designing advanced electrocatalytic materials. Chen et al. [121] used ionic liquid (IL) as Shuang Yuan of Fe and P to prepare iron phosphate by microwave irradiation. Moreover, CNTs play a dual role: they facilitate the formation of iron phosphate NPs (Figure 7a) and enhance the conductivity of the catalyst, thereby improving its catalytic performance (Figure 7b,c). Iron-based catalysts are prone to oxidation–induced deactivation, which can be mitigated through CNTs encapsulation. Yu et al. [122] used iron NPs encapsulated by N-CNTs as the integrated electrode of HER on foamed iron, and achieved an η of 525 mV at a current density of 10 mA cm^{-2} (Figure 7d–f). This electrocatalyst also exhibits excellent HER performance across different pH levels (Figure 7g).

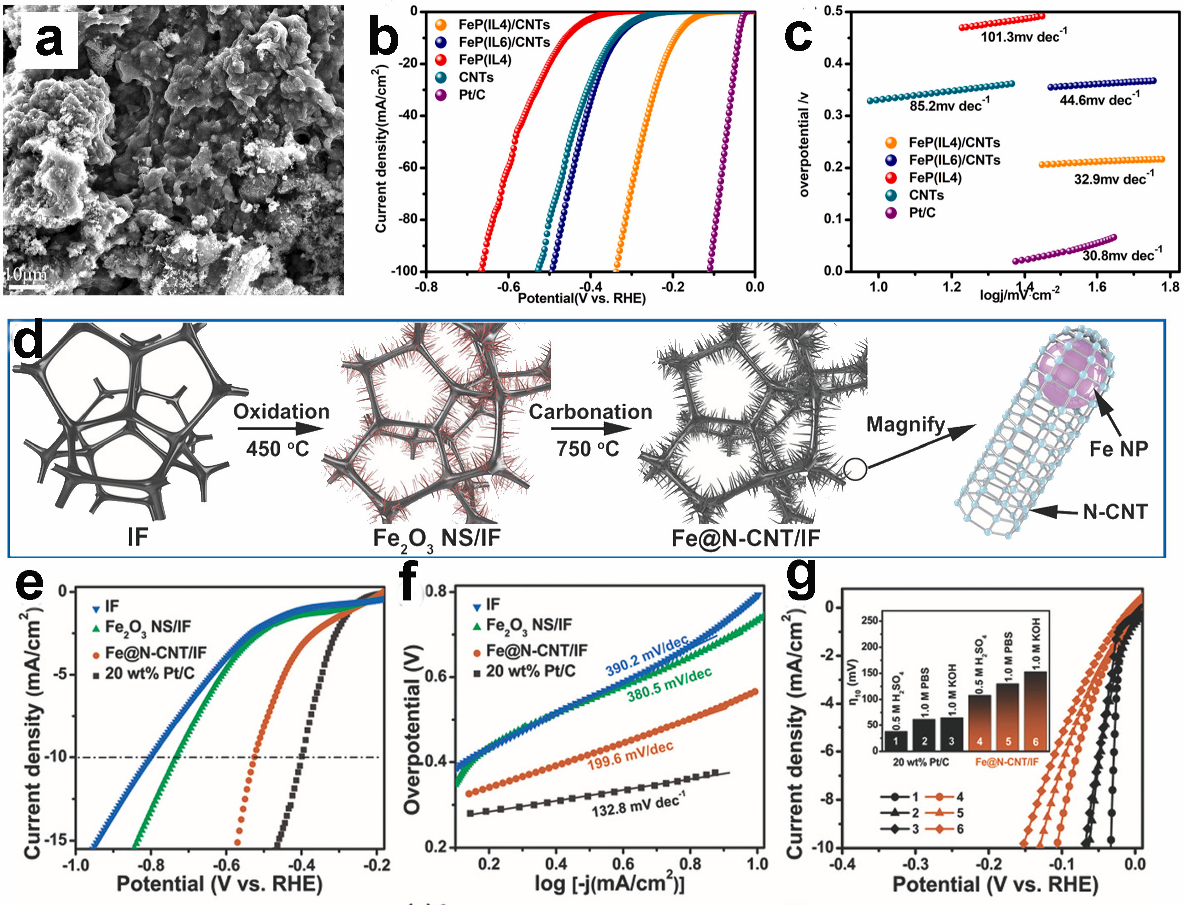

Figure 7. (**a**) SEM image of FePO(IL4)/CNTs (**b**) LSV curves and (**c**)Tafel slope updated from reference [121]. King Saud University. (**d**) Schematic diagram of the synthesis process of Fe@N-CNT/IF. (**e**) Polarization curves and (**f**) Tafel slope of IF, Fe_2O_3 NS/IF, Fe@N-CNT/IF, and 20 wt% Pt/C in 0.5 m Na_2SO_4, respectively. (**g**) Polarization curves for HER in traditional all-pH electrolytes updated from reference [122]. 2019, WILEY.

3.2.2. Co/CNTs Composite Catalysts

The electrocatalytic HER performance of Co has garnered considerable research interest in the field of transition metal-based materials in recent years. While conventional volcano plot relationships indicate Co possesses strong hydrogen intermediate (H_{ad}) binding energy, its HER activity remains substantially lower than PGMs positioned at the volcano peak. By adjusting the electronic structure and geometric structure of the active center, the performance of Co-based catalyst was optimized to make it have catalytic activity and stability similar to Pt. In alkaline electrolyte, the strong oxygen affinity of Co is beneficial to accelerate the dissociation of water before H_{ad} is adsorbed by Volmer step, because water molecules are proton donors. Accordingly, the last decade has seen significant advances in synthesizing Co-based catalysts spanning alloys, oxides, and chalcogenides [123–126]. The catalytic efficiency can be further enhanced by systematically tuning key parameters: electronic states, band structures, adsorption energetics, conductivity, surface area, and active site density [127,128]. However, its poor conductivity and insufficient exposure of active sites are still the only factors restricting its practical application.

CNTs have clear channel structure and large specific surface area, which is beneficial to the transfer of electrons and mass [129]. Combining with CNTs can not only obtain larger electrochemical active area and improve conductivity, but also anchor metal compounds. Zou et al. [130] reported the synthesis of cobalt-rich nitrogen-doped carbon nanotubes (Co-NRCNTs), which can effectively catalyze the HER with activity close to that of Pt. Due to the coating of CNTs on cobalt, the corrosion of electrolyte on the catalyst is greatly reduced. CNTs have nitrogen doping and defect-rich structures, which have good restraint and protection effects. N-rich doping enhances CNTs' electrical conductivity while simultaneously generating abundant active sites for HER electrocatalysis [131]. Unlike doping CNTs, modifying Co is also an important method to enhance hydrogen evolution activity. Co phosphide exhibits near-optimal H_{ad} binding energy at proton-accepting sites, making it a highly promising HER catalyst [132,133].

Cai et al. [134] synthesized Co_2P/Co_4N/CNTs composite using zeolite pyrazole acid skeleton -67 (ZIF-67) as self-sacrifice template. The composite catalyst demonstrates exceptional HER activity due to the cooperative effects between Co_4N and Co_2P phases, abundant exposed active sites, and the superior charge transport capability of CNTs ($\eta_{100} = 228$ mV). Yan et al. [135] proposed an integrated coordination-polymerization strategy to prepare Co@N-CNT@g-C_3N_4, and carried out an effective HER at all pH values. Importantly, Co particles, CNTs and g-C_3N_4 are skillfully assembled at the same time, and a tightly integrated interface is constructed, thus improving the electron transfer efficiency. Yang et al. [136] successfully prepared a HER electrocatalyst coupling Co nanoparticles with N–doped carbon nanotubes/graphitic nanosheets (Co@NCNTs/NG) through a high-temperature pyrolysis method. In Co@NCNTs/NG-1, the NCNTs are interspersed in a manner that promotes thorough contact among different phases (Figure 8a,b). This arrangement not only accelerates the transfer of electrons and reaction species throughout the reaction but also prevents the aggregation of Co nanoparticles, thereby enhancing stability. Co@NCNTs/NG–1 exhibits outstanding HER performance in 1 M KOH solution (Figure 8c–e). Co@NCNTs/NG-1 demonstrates a stable potential for 50 hours at a constant current density of 50 mA cm^{-2} (Figure 8f), indicating exceptional stability under alkaline HER conditions. Indeed, the interaction between Co nanoparticles and NCNTs plays a crucial role in enhancing HER electrocatalytic activity. The tight anchoring of cobalt nanoparticles on NCNTs effectively suppresses their aggregation during pyrolysis. Moreover, the strong interaction between Co nanoparticles and NCNTs contributes to the improved durability of Co@NCNTs/NG-1 in HER applications.

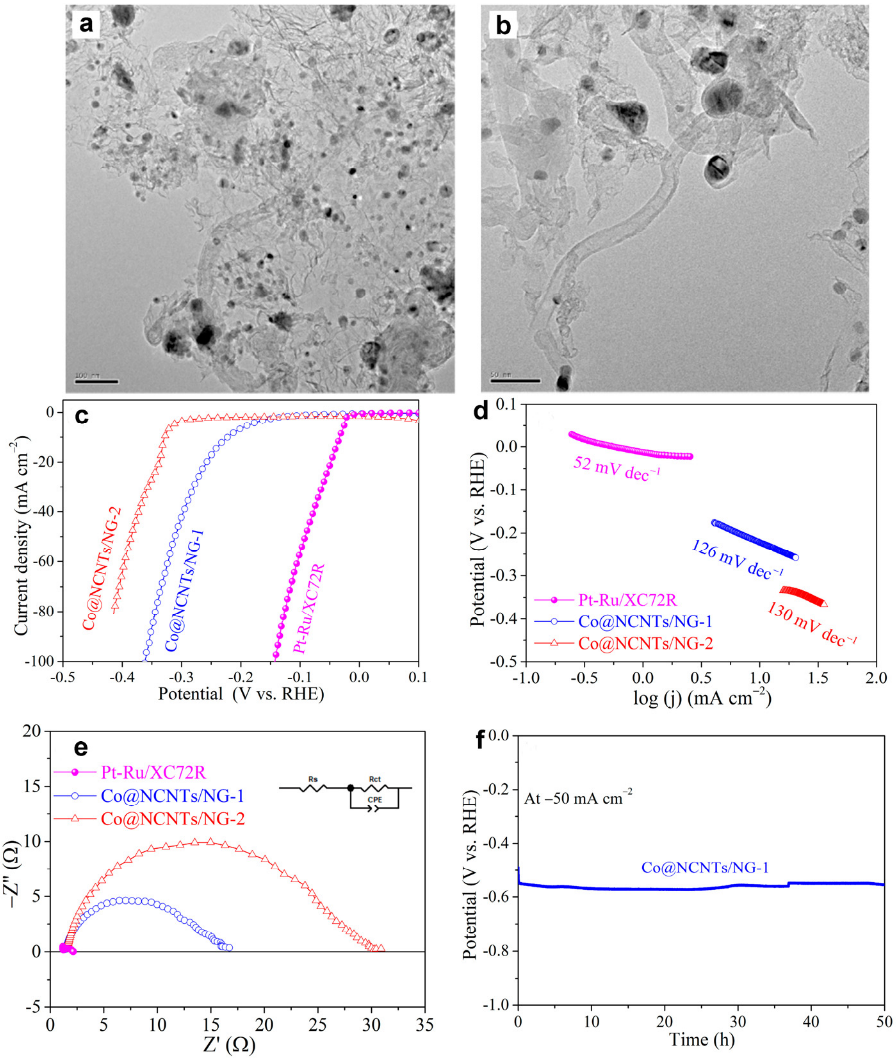

Figure 8. TEM images with different magnifications of (**a**,**b**) Co@NCNTs/NG-2, (**c**) LSV, (**d**) Tafel slope, (**e**) EIS, (**f**) the current–time curve updated from reference [136]. 2023, MDPI.

3.2.3. Ni/CNTs Composite Catalysts

Ni is one of the non-precious metals in group 10, with atomic number 28 and silvery white appearance. Its valence is 0, 1, 2 or 3, and it is one of the most promising Pt substitutes. It is the fifth most abundant element on the earth, and it is cheaper. For more than ten years, Ni has been widely used as HER electrocatalyst, especially in alkaline medium, because of its good catalytic activity, good corrosion resistance in hot concentrated alkaline solution and more stability than Fe and Co [137]. However, due to its high η and Tafel slope, pure Ni is not an effective electrocatalyst, but its electrocatalytic activity can be improved through nanostructures, which include making nano-sized Ni particles to increase its surface area. Other methods include preparing Ni alloys such as $NiAl_3$, Ni_3Al, NiMo, NiCo and NiFe, and doping heteroatoms such as N and P, can reduce adsorption energy, accelerate hydrolysis, provide sufficient protons and improve hydrogen production. The doping of carbon nanostructures such as CNTs improves the dispersibility and conductivity of the catalyst [138]. Wang et al. [139] synthesized Ni NPs encapsulated by N-doped bamboo CNTs by one-pot pyrolysis at low temperature. The incorporation of metallic Ni facilitated the conversion of the catalyst carrier from PCN to N-doped carbon, thereby markedly enhancing charge transfer efficiency. The coexistence of multiphase Ni, N-rich doping, and compartmentalized CNTs morphology creates a high density of active centers, enabling efficient alkaline HER catalysis. Ni/NC-0.35 shows the best electrocatalytic stability and activity with η_{10} of 133 mV. Yan et al. [140] demonstrated a simple template participation strategy, which was used to directly grow Ni NPs and N-doped CNTs on carbon nanorod substrates *in situ* to form hierarchical branching structure (Ni@N-CNT/NRs). The meticulous design of this unique layered structure not only increases the surface area but also reduces the charge transfer resistance and enhances mechanical robustness. The list of HER electrocatalysts for Fe, Co and Ni-based CNTs composites is shown in Table 2.

Table 2. Fe, Co and Ni/CNT composite electrocatalysts for HER.

Material	η_{10}/mV	Tafel Slope (mV·dec^{-1})	Stability	Electrolyte	Reference
CoP/CNT	122	54	18 h	0.5 M H_2SO_4	[129]
NRCNTs	260	40	——	0.5 M H_2SO_4	[130]
$Co_2P@Co_2P/Co$-POM/NF	130	135	40 h	1 M KOH	[132]
Co_2P/Co_4N/CNTs	228 (η_{100})	124	50 h	1 M KOH	[134]
P-Fe_3O_4/IF	138 (η_{100})	41.9	60 h	1 M KOH	[119]
Co@N-CNT@g-C_3N_4	61	88	1000 cycles	1 M KOH	[135]
Ni@N-CNT/NRs	134	98.3	1000 cycles	0.1 M KOH	[140]
Ni/NC-0.35	133	1.9	16 h	1 M KOH	[139]
Fe@N-CNT/IF	525	199.6	10 h	0.5 M Na_2SO_4	[122]
NiS@CNTs	280	102	500 min	1 M KOH	[141]
Co_4N@CoSA/N-CNT/CC	86	82.2	5000 cycles	1 M KOH	[59]
FePO(IL4)/CNTs	185	32.9	16 h	0.5 M H_2SO_4	[121]
CNT-f-FeP^{F}	457	67.9	12 h	0.1 M H_2SO_4	[118]
Co-NCNTs-10	103/204/337	50	20 h/20 h/20 h	0.5 M H_2SO_4/PB/1 M KOH	[131]
$2Fe_3O_4$@N-HCNT@$2Fe_3O_4$@DCL	——	100.63	1000 cycles	1.0 M KOH	[120]
CNT@NiSe/SS-400	174	135	——	1.0 M KOH	[35]
Ni-$Ni_{12}P_5$@CNT/rGO-0.5	217.4	55.43	10 h	0.5 M H_2SO_4	[142]
$2Fe_2S$/CNT	930	179.3	12 h	0.1 M PBS	[143]
MWCNTs@TpPa-COF@Co/CoO	28.8	69.07	2000 cycles	1.0 M KOH	[144]
CoS_2-NCNHP	158/192	84/95	24 h	0.5 M H_2SO_4/1.0 M KOH	[145]
CNT-f-1^{adt}	778	162	12 h	0.05 M PBS	[146]
NFP@NC	206	91	50 h	seawater	[147]
Ni/NCT	199/202/212	133.37/135.4/1356.5	50 h	1.0 M KOH/1.0 M KOH + 0.5 M NaCl/1.0 M KOH + seawater	[148]
Ni-N-C/Ni@CNT-H	175	97.24	160 h	1.0 M KOH	[149]
CoPi/PF-CNTs	105	32	24 h	0.5 M H_2SO_4	[150]

3.3. Polymetallic and Alloy/CNTs Composite Catalysts

Recently, a lot of work has been devoted to the manufacture of TMs and their derivatives for HER electrocatalysis. These studies demonstrate that alloy-type TMs (e.g., NiCo, FeCo and FeNi) exhibit substantially improved catalytic activity relative to monometallic systems, attributable to electronic structure modulation, reduced activation barriers, and accelerated reaction kinetics through synergistic effects. The FeNi alloy system is particularly remarkable as Fe doping cooperatively tailors the electronic structure of Ni sites and fine-tunes reactant adsorption energetics, thereby significantly enhancing electrocatalytic performance [151]. However, the intrinsic ferromagnetism and chemical instability of bare FeNi alloys under harsh conditions lead to severe nanoparticle aggregation and consequent active site loss. Consequently, a precisely controlled synthetic strategy is crucial to ensure robust immobilization of metal species while preventing FeNi nanoparticle aggregation.

NCNTs exhibit ideal properties for electrocatalysis: large accessible surface areas, strong charge-transfer capability, minimal diffusion resistance, and remarkable mechanical durability. This strategy significantly enhances the alloy's electrical conductivity while simultaneously protecting active particles from corrosion and detachment through encapsulation effects. The coupling of NCNTs with HER-active FeNi modulates the electronic configuration and lowers the energy barrier for favorable adsorbate binding, thereby achieving concurrent high activity and stability. Therefore, it is a promising method to embed NiFe alloy particles in NCNTs, which can meet the application requirements of electrode catalysts in electrolytic cells. To sum up, Zhang et al. [152] developed a simple and efficient method to prepare N-doped CNTs encapsulated FeNi alloy nanoparticles (FeNi@NCNTs). The experimental results show that the Fe_1Ni_4@NCNTs material has the highest activity and durability in HER. NCNTs' self-catalyzing hierarchical design optimally exposes active sites while minimizing electron transport distances, thereby amplifying catalytic synergy. Fe doping simultaneously enhances the intrinsic catalytic activity of metallic Ni through electronic modulation. This work establishes a foundational strategy for developing alloy-based catalysts with exceptional activity and stability for overall water splitting applications. Optimizing the performance of monoatomic catalysts has been a hot topic in recent years, but achieving the synergistic effect of diatomic catalysts remains a significant challenge.

Recent years have witnessed substantial advancements in non-precious metal HER catalysts through extensive investigations. Shakir et al. [153] synthesized a ternary composite of CNTs-coated $CoFe_2O_4$/CoFe LDH (CoF/CoFe LDH@CNTs) using hydrothermal and ultrasonic methods. The SEM image in Figure 9a reveals a stacked plate/sheet-like morphology along with nanoparticles of CoF/CoFe LDH. Following the formation of the CoF/CoFe LDH@CNTs composite (Figure 9b), the CoF/CoFe LDH appears uniformly wrapped by thin, thread-like CNTs, suggesting strong interfacial bonding between the components due to the ultrasonic-assisted synthesis. CoF/CoFe LDH@CNTs exhibits the lowest η and Tafel slope values, indicating superior HER performance compared to other electrocatalysts (Figure 9c,d). Among these, transition metal/nitrogen-doped carbon-based materials (TMs/NC), particularly cobalt/nitrogen-doped carbon (Co/NC) materials [154], have shown excellent catalytic activity. They are considered one of the most promising candidates to replace current advanced precious metal-based catalysts for renewable energy technologies. Hu et al. [155] synthesized RuM (M = Cu, Rh, and Pd) alloy NPs via nanosecond laser ultrafast confined alloying (LUCA). In summary, the sufficient incorporation of non-precious metals in the alloy significantly reduces catalyst costs while maintaining or even enhancing the intrinsic activity of the alloyed catalyst. The integration of CNTs with Cu NPs, Ru NPs, and RuCu alloy NPs significantly enhanced the catalytic activity, following the order: RuCu > Ru > Cu NPs, demonstrating the synergistic effect of RuCu alloy in boosting HER performance (Figure 9e–g). Figure 9h,i demonstrate that the incorporation of Cu not only accelerates water dissociation to provide more protons for subsequent reactions, but also facilitates H adsorption/desorption. Figure 9j reveals a negative shift in the Hupd peak potential for $Ru_{95}Cu_5$/CNTs (0.061 V) compared to Ru/CNTs (0.076 V), suggesting that the improved HER performance stems from moderated hydrogen chemisorption strength, which promotes more efficient hydrogen desorption. These studies have promoted the development of TMs-based CNTs composites in hydrogen evolution. The HER electrocatalysts for polymetallic and alloy/CNTs composites are shown in Table 3.

Table 3. Polymetallic and alloy/CNT composite catalysts for HER.

Material	η_{10}/mV	Tafel Slope (mV·dec^{-1})	Stability	Electrolyte	Reference
Co@Zn-N-CNTs	67	52.1	50 h	0.5 M H_2SO_4	[156]
$Ni_3ZnC_{0.7}$/Ni@CNTs	93	116.23	400 h	1.0 M KOH	[157]
Co/Co_3ZnC^{-2}	261/226	99.8/119.5	30 h	0.5 M H_2SO_4/1.0 M KOH	[158]
NiCo-N-CNTs-900	54	40.6	2000 cycles	1.0 M KOH	[159]
Pt_3 Co@NCNT	42	27.2	35 h	0.5 M H_2SO_4	[160]
c-CNT-0.68@TpBpy-Ru	112	160	12 h	1.0 M KOH	[113]
FeNi@NCNTs	279	118	20 h	1 M KOH	[152]
CoFe@NC/$CoFe_2O_4$/IF	66	49.45	72 h	1.0 M KOH	[161]
$CoFe_2O_4$/MWCNTs/IL	——	172	5 h	PB	[162]
Ru - PtFeNiCuW/CNTs	16	27.9	50 h	1.0 M KOH	[163]
Pt@MC-VA	208 (η_{500})	28	24 h	0.5 M H_2SO_4	[114]
$(PtNi)_{55}$(-TiZrHf)$_{45}$/CNT	11	37.73	58 h	0.5M H_2SO_4	[164]
NiRu-CNTs	5.4	31.3	10 h	1.0 M KOH	[165]
$Ru_1Co_{1.5}$@OCNT-700	17.6	35.78	2000 cycles	1.0 M KOH	[166]
Mo-Ru/CNTs	34.8/44.9	32.5/33.4	100 h	1.0 M KOH/seawater	[167]
RuCo NPs/CNTs-400°C	39/27	32/27	24h	0.5 M H_2SO_4/1.0 M KOH	[168]

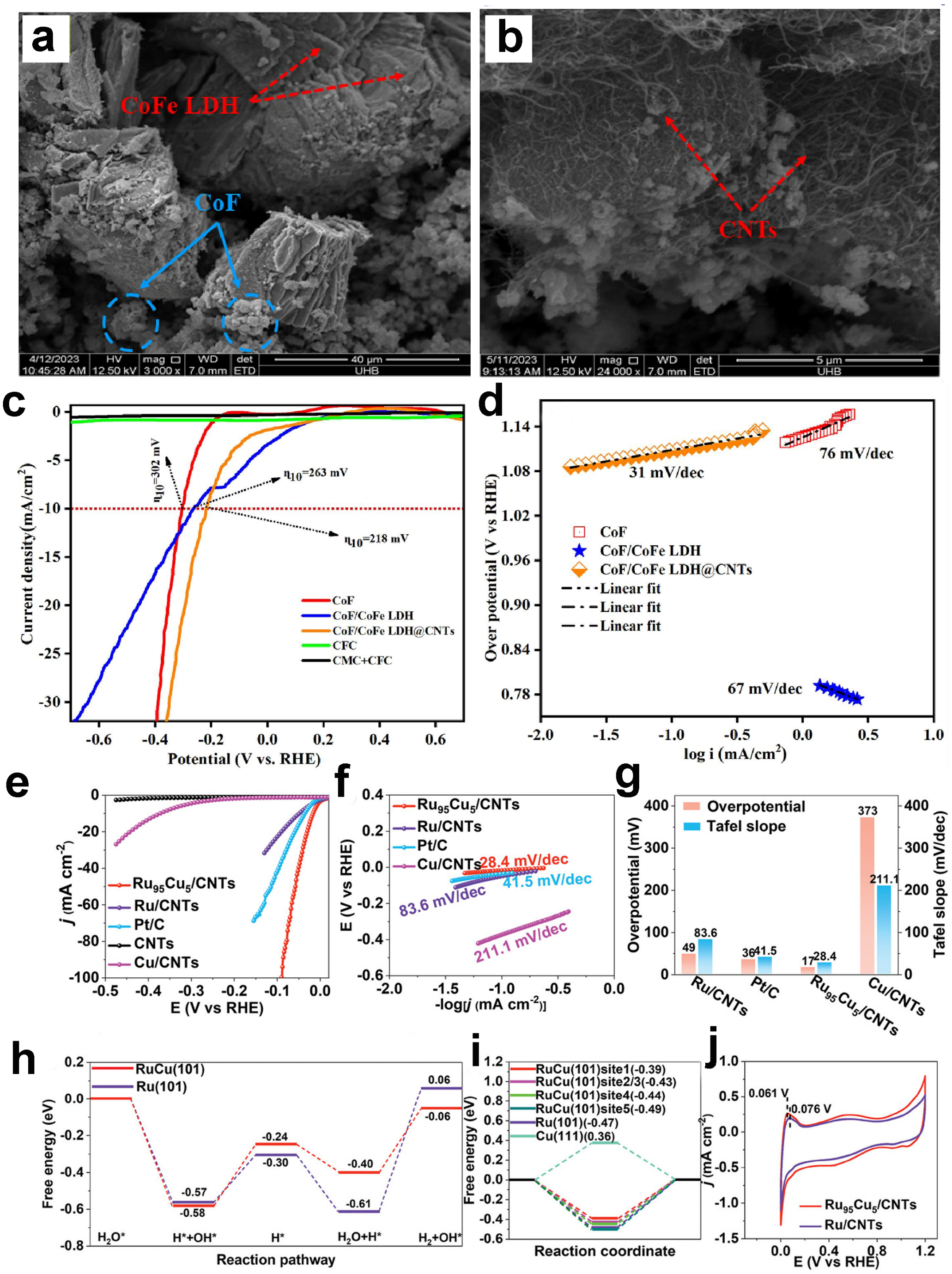

Figure 9. SEM images of (**a**) CoF/CoFe LDH and (**b**) CoF/CoFe LDH@CNTs (**c**) LSV curve (**d**) Tafel slope of electrocatalysts updated from reference [153]. 2024, Elsevier. (**e**) LSV curves, (**f**) Tafel slopes, (**g**) Summarized overpotentials and Tafel slopes. (**h**) Free energy diagrams of the elementary steps in alkaline HER for Ru (101) and RuCu (101). (**i**) Adsorption free energies of H for 5-site of RuCu (101), Ru (101), and Cu (111). (**j**) CV curves of $Ru_{95}Cu_5$/CNTs, and Ru/CNTs updated from reference [155]. 2025, WILEY.

3.4. The Environmental Impact of HER Results

The HER reaction process includes two steps: the Volmer step and either the Tafel step or the Heyrovsky step [169]. In the case of an acidic electrolyte, the first step of the Volmer reaction involves the electrochemical discharge to form an adsorbed hydrogen intermediate (H*) on the active site. Subsequently, adjacent adsorbed H* intermediates combine to generate H_2 (Tafel reaction). Alternatively, the adsorbed H* can combine with a proton, accompanied by an electron transfer reaction to produce H_2 (Heyrovsky reaction) [11]. The HER process in alkaline environments also involves the dissociation of water, which leads to the need for more energy. In practical applications, it is highly desirable for ideal electrocatalysts to operate under harsh conditions. Therefore, the design and development of highly efficient pH-universal HER electrocatalysts is essential. Recently, TMs-based catalysts have been reported, but these catalysts are susceptible to acid and alkali corrosion [99]. Chen et al. [170] designed Co@CNTs|Ru catalysts demonstrate exceptional pH-universal activity, delivering 10 mA cm^{-2} at ultralow overpotentials (10 mV alkaline, 32 mV acidic, 63 mV neutral) with 50-h durability, where CNTs effectively prevent catalyst corrosion. In summary, CNTs not only protect TMs from acid/alkali corrosion but also provide spatial nanoconfinement to enhance electron/charge transfer, making them an ideal choice for developing pH-universal HER electrocatalysts.

4. Summary, Challenges and Perspectives

4.1. Summary of This Review

A series of important progress has been made in the research of TMs/CNTs composites in the field of electrochemical HER. These composites have become potential catalysts for efficient HER because of their excellent conductivity, good catalytic activity and large specific surface area. This review summarizes three common synthesis methods for TMs/CNTs composite catalysts and recent research progress in their application for water-splitting hydrogen production. The results demonstrate that CVD can effectively enhance catalyst stability and is suitable for large-scale synthesis. Heteroatom doping can further enhance the electrical conductivity of CNTs while effectively improving their affinity for TMs, thereby boosting the HER catalytic performance of the resulting catalysts.

4.2. Challenges and Perspectives

Although the current research results are encouraging, there are still some challenges and unsolved problems that need to be further discussed in future research.

1. Improvement of catalytic activity: Further explore the selection and proportion of TMs and enhance the catalytic activity by synthesizing new alloys or compounds. At the same time, other doping elements or modification methods can be considered to improve the catalytic performance of the composites.
2. Structural design optimization: By adjusting the morphology and structure of CNTs, studying the interaction between TMs and CNTs, and determining the optimal interface design for further promoting charge transfer and reaction kinetics.
3. Study on durability and stability: In large-scale applications, the durability and stability of catalysts are very important. In the future, more systematic long-term tests are needed to understand the performance degradation mechanism of composite materials in the actual electrochemical HER process.
4. Environmental friendliness: With the requirement of sustainable development, how to reduce the cost of catalysts and improve the environmental friendliness of its production process will be an important research direction. This may involve the utilization of renewable resources and the development of green synthesis methods. In addition to the field of electrochemical HER, TMs/CNTs composites also have the potential to be applied to other electrochemical reactions, such as batteries and fuel cells. Expanding the application fields of these materials will have a positive impact on the development of energy conversion and storage technology. The study of TMs/CNTs composites in electrochemical HER is still full of opportunities and challenges. Through continuous innovation and exploration, it is expected to achieve more efficient and economical HER production in the future and contribute to the development of sustainable energy.
5. In the research of TMs/CNTs composites for electrochemical HER is expected to promote the further development of this field by combining Machine learning (ML) with experimental and theoretical research. ML can efficiently analyze a large number of material data and identify the key factors affecting catalytic performance. By constructing ML model, the catalytic activity of different combinations of TMs and CNTs can be predicted, thus guiding the synthesis and optimization of materials. This can greatly reduce the number of experiments and speed up the development process. By analyzing the experimental data, ML model can identify the key steps, such as the reaction path and transition state, and provide a deeper understanding of the catalytic process. This is very important for designing more efficient catalysts. Combining ML with the electrochemical hydrogen evolution of TMs-based CNTs composites can not only accelerate the discovery and optimization of new materials but also provide deeper understanding and rich data support for research.

Author Contributions

Conceptualization, J.Z., L.Z. and L.J.; Methodology, Y.Y.; Software, Q.Z.; Formal Analysis, J.Z.; Investigation, J.Z.; Resources, J.Z. and G.Z.; Data Curation, G.Z.; Writing—Original Draft Preparation, J.Z.; Writing—Review & Editing, G.Z.; Visualization, L.Z.; Funding Acquisition, G.Z.

Ethics Statement

Not applicable.

Informed Consent Statement

Not applicable.

Data Availability Statement

Not applicable.

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Declaration of Competing Interest

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

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