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Research Progress of Gold-based Catalysts for Hydrogen Evolution Reaction

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Abstract

The hydrogen evolution reaction (HER) is a critical step in the process of electrolytic water splitting for hydrogen production. The effectiveness, durability and economy of electrocatalysts are necessary prerequisites for meeting performance expectations. The unique electronic structure of gold enables gold-based catalysts to exhibit excellent properties in hydrogen evolution reactions. This review outlines the fundamental mechanisms of HER and the characteristics of gold-based materials. Furthermore, the effects of alloying strategy, carrier synergistic, and atomically precise construction of gold are deliberated. Finally, the future prospects involved in this process are discussed. We hope that this review can provide valuable insights for the design and development of efficient and stable catalysts for applications in electrochemical hydrogen production and other related fields.

Keywords

Gold-based catalysts; Hydrogen evolution reaction; Alloying strategy; Carrier synergistic; Atomically precise construction.

1. INTRODUCTION

Global energy demand is undergoing unprecedented growth, particularly against the backdrop of the third energy revolution, which is characterized by low-carbon, carbon-free, and sustainable energy sources. Hydrogen energy, recognized as an energy carrier with high energy density and clean combustion products, is playing an increasingly significant role in building the future energy system [1]. Electrolytic water hydrogen production, particularly the technology driven by renewable energy, represents the core pathway for large-scale production of green hydrogen, with its essence lying in efficient, stable, and economical electrocatalysts [2]. Currently, platinum (Pt)-based catalysts are regarded as the benchmark materials for the hydrogen evolution reaction (HER) in acidic media, however, their high cost and scarcity severely limit the widespread application of electrolytic water technology [3]. Therefore, the development of new catalysts that can either replace or significantly reduce the use of precious metals has become an urgent need to promote the development of the hydrogen energy economy.

Gold-based catalysts, compared to other precious metal-based catalysts, exhibit a series of unique advantages. Firstly, gold (Au) possesses excellent corrosion resistance, especially in acidic environments. This characteristic enables it to maintain both structural and chemical stability during prolonged electrolysis processes, thereby extending the catalyst's lifespan [4]. Secondly, the d-band center position of gold enables it to adsorb hydrogen moderately, neither too strongly nor too weakly. This characteristic aids in balancing the adsorption and desorption steps during the hydrogen evolution reaction, optimizing the reaction kinetics. The performance of gold-based catalysts in alkaline conditions is equally remarkable, as they exhibit good activity and stability in high pH environments, thus broadening their applicability in water electrolysis for hydrogen production [5]. Additionally, the surface electronic properties of gold can be adjusted through simple chemical or structural modifications, such as forming alloys or doping with non-metallic elements, which further enhances its electronic structure and catalytic activity.

Another advantage of gold-based catalysts is their unique surface plasmon resonance effect, which can enhance local electric field intensity, promote charge transfer processes, and thereby improve hydrogen evolution efficiency under specific conditions [6]. Moreover, the nanostructure of gold is easily tunable; by altering its size, shape, and dispersity, one can effectively regulate its surface electronic states and the density of active sites. In terms of environmental compatibility, gold, being a non-toxic metal, offers advantages in biocompatibility and environmental friendliness, making gold-based catalysts more attractive in applications where environmental and health impacts are a consideration [7].

This review aims to systematically summarize recent research progress on gold-based catalysts for HER, thoroughly addressing multi-scale and multi-dimensional structural design and regulation, ranging from macroscopic alloys to atomic-level single atoms and nanoclusters. Additionally, it provides an outlook on the challenges and future development prospects in this field, with the goal of offering valuable references and insights for the design and development of novel, efficient hydrogen evolution catalysts.

2. FUNDAMENTAL MECHANISMS

The hydrogen evolution reaction (HER) is one of the key steps in the process of water splitting for hydrogen production, primarily occurring at the cathode. HER involves the process where protons (H^+) accept electrons at the cathode and are reduced to generate hydrogen gas (H_2). This process can proceed through two main electrochemical reaction mechanisms: the Volmer-Heyrovsky mechanism and the Volmer-Tafel mechanism.

(1)Volmer step: $H^+ + e^- + * \rightarrow H_{ads}$

Protons are adsorbed on the catalyst surface to form adsorbed hydrogen (H_{ads}), where * represents the active site on the catalyst surface.

(2)Heyrovsky step: $H_{ads} + H^+ + e^- \rightarrow H_2 + *$

Adsorbed hydrogen combines with protons in the solution to generate hydrogen gas, which is then released into the solution.

(3)Tafel step: $H_{ads} + H_{ads} \rightarrow H_2 + 2*$

Involves the direct combination of two adsorbed hydrogen atoms to form hydrogen gas, which is then released into the solution.

In these reaction steps, the formation and desorption of adsorbed hydrogen are crucial steps in HER kinetics, and their rates directly affect the efficiency of hydrogen production through water electrolysis. Therefore, the design of catalysts aims to optimize these steps to enhance the rate and efficiency of HER.

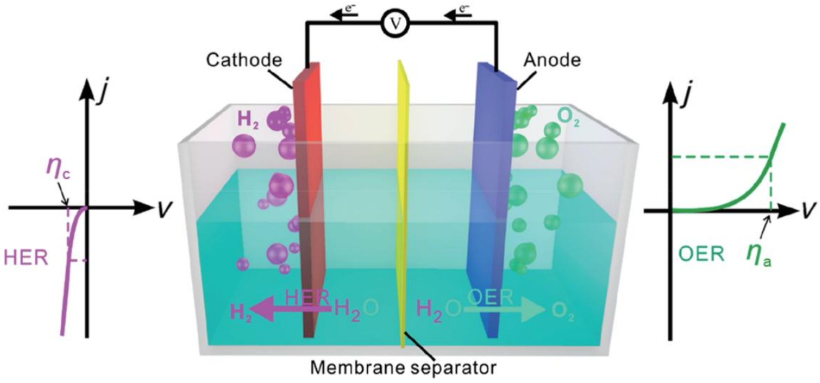

Figure 1. Hydrogen evolution reaction and oxygen evolution reaction for water splitting [8].

3. CHARACTERISTICS OF GOLD-BASED MATERIALS

Gold-based materials have emerged as promising catalysts for HER, a process crucial for sustainable hydrogen production. In recent years, significant research efforts have been dedicated to exploring the potential of gold-based catalysts. The activity of these materials in HER during water electrolysis is closely related to their electronic structure. The d-band center position of gold determines the strength of its interaction with hydrogen atoms, directly influencing the adsorption and desorption behaviors of hydrogen [9]. By regulating the electronic structure of gold-such as the d-band center position, surface electronic states, and coordination environment-the adsorption energy of hydrogen can be optimized, thereby improving hydrogen evolution activity. Specifically, the coordination geometry of gold atoms, exposed crystal facets, and surface defects all affect the local electron density distribution, which modulates the Gibbs free energy of hydrogen adsorption (ΔG_{H^*}) [10]. An ideal gold-based catalyst should possess moderate hydrogen adsorption energy to balance the adsorption and desorption processes, facilitating rapid electron transfer and efficient hydrogen evolution kinetics.

Furthermore, the electronic structure of gold-based materials can be regulated through alloying, doping, or surface modification to further optimize their hydrogen evolution activity. In conclusion, a deep understanding of the relationship between the electronic structure of gold-based materials and their hydrogen evolution activity is crucial for designing and develoing efficient and low-cost electrocatalysts for water splitting hydrogen evolution.

4. ALLOYING STRATEGY

Alloying gold with other metallic elements is a classic and effective strategy to break its intrinsic catalytic inertness and enhance hydrogen evolution performance. This leap in performance arises not merely from the simple summation of the properties of the two metals, but rather from intricate electronic and geometric effects. These effects work synergistically to finely regulate the electronic structure and atomic arrangement on the catalyst surface, thereby optimizing the adsorption energy for key intermediates (H) in the hydrogen evolution reaction. According to the Sabatier principle of the HER, an ideal catalyst should have an adsorption free energy for hydrogen atoms (ΔG_{H^*}) close to 0 eV, as both excessively strong and weak adsorption can lead to an increase in the reaction energy barrier [11]. The core of designing gold-based alloys lies in the precisely regulating the d-band electronic structure of Au sites to achieve the optimization of ΔG_{H^*} by introducing a second or third metal component. The electronic effect pertains to the charge transfer between alloy components due to differences in electronegativity [12]. This redistribution of charge alters the work function and the position of the d-band center on the catalyst surface, thereby influencing the binding strength of adsorbates. The geometric effect involves lattice strain caused by the mismatch in atomic radii, as well as the specific active site ensembles (atomic clusters) formed by different atoms on the surface [13]. These factors collectively modify the adsorption configurations of reactants and intermediates on the catalyst surface and the activation energy barriers.

Among numerous gold-based alloy systems [6], the gold-ruthenium (Au-Ru) alloy has garnered significant attention due to its excellent bifunctional catalytic activity and remarkable stability in acidic environments [14]. Ruthenium (Ru), as a relatively low-cost platinum group metal, not only exhibits good intrinsic hydrogen evolution activity but also its oxide (RuO_2) serves as an efficient catalyst for the oxygen evolution reaction (OER). However, pure ruthenium-based catalysts exhibit poor stability during the acidic water electrolysis process, being prone to dissolution or oxidative deactivation. Research has shown that the introduction of gold into ruthenium-based materials to form Au-Ru alloys can significantly enhance the overall performance of the catalyst. A pioneering study successfully prepared an Au-Ru alloy catalyst with a nanofiber structure through a strategy involving electrospinning and high-temperature calcination reduction. In the hydrogen evolution reaction, Au-Ru alloy nanofibers exhibit superior activity and stability compared to pure Ru, Au, and commercial Ru/C catalysts. More importantly, the catalyst demonstrates excellent long-term stability in acidic media, which is in stark contrast to the easily deactivated pure Ru-based catalysts. Theoretical calculations (DFT) further reveal that the alloying of Ru with a small amount of Au not only stabilizes the catalyst's structure but also optimizes the adsorption energy of H* through electronic effects, thereby enhancing HER kinetics [15]. This enhancement in stability is crucial for acidic electrolyzed water, as the harsh environment of strong acids and high potentials imposes stringent demands on the durability of catalysts. The introduction of Au is believed to alter the redox behavior of Ru, inhibiting its excessive oxidation and thereby maintaining the stability of the catalytic active sites. The study also highlights that these Au-Ru alloy nanofibers perform exceptionally well in overall water splitting (OWS), surpassing the performance of most Ru-based bifunctional catalysts reported in the literature, demonstrating significant potential as practical catalysts for acidic electrolyzed water. Au alloying is an effective approach for constructing highly efficient and stable acidic water electrolysis catalysts [16], and its success is attributed to the synergistic electronic effects between Au and other metal, as well as the stabilizing effect of Au on the matrix.

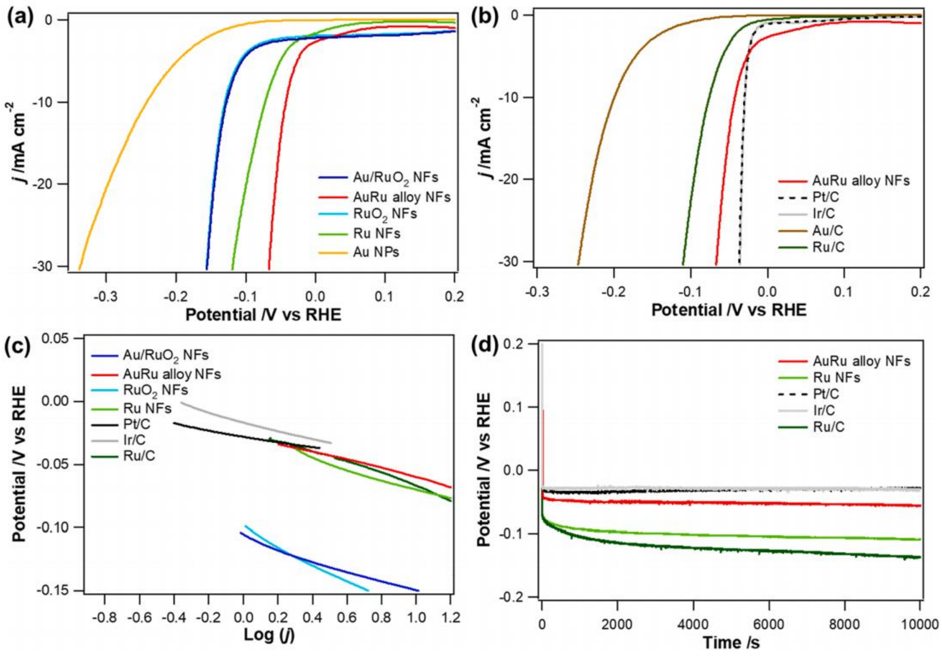

Figure 2. Comparison of the HER catalytic activities of various Au-Ru catalysts [14]

5. CARRIER SYNERGISTIC EFFECT

In multiphase catalysis, the interaction between the active component and the support (Metal-Support Interaction, MSI) is one of the key factors determining the final performance of the catalyst. For gold-based catalysts, selecting an appropriate support and meticulously engineering its interface not only provides physical support and prevents the agglomeration of the active component but, more importantly, profoundly influences the electronic structure and catalytic activity of the gold sites through charge transfer, chemical bonding, and strain effects at the interface. This synergistic effect can transform a material with inherently low activity into a highly efficient catalyst or push a material with higher activity to its ultimate performance.

Metal-Organic Frameworks (MOFs) are widely used as catalyst supports or catalyst precursors due to their ultra-high specific surface area, tunable pore structures, and diverse combinations of metal nodes/organic ligands. A study successfully encapsulated gold nanoparticles (Au NPs) in situ into the pores of a zinc-based MOF (Zn-MOF), forming an Au@Zn-MOF composite material [17]. This composite material exhibited electrocatalytic activity for both the oxygen reduction reaction (ORR) and the hydrogen evolution reaction (HER) under acidic conditions. In HER, the onset potential of Au@Zn-MOF is only 0.02 V (vs. RHE), demonstrating a favorable synergistic effect between Au NPs and the Zn-MOF support. The ordered pore structure of MOF may facilitate the mass transfer of reactants and the rapid desorption of the product (H_2), while its organic ligands may also interact electronically with Au NPs, thereby modulating their catalytic performance. However, the study also found that in O_2-saturated solutions, the Tafel slope of HER significantly increases, indicating competitive adsorption between protons and O_2 on the electrode surface, which reveals the importance of understanding interfacial behavior in complex electrochemical environments. MOFs exhibit great potential as carriers, but their generally poor conductivity limits their direct application in electrocatalysis. In the future, combining MOFs with conductive materials (such as carbon nanotubes and graphene) or converting them into derived carbon materials through pyrolysis may be effective ways to overcome this limitation.

Two-dimensional materials, especially transition metal dichalcogenides (TMDs, such as MoS_2) and graphene, have become ideal carriers for gold-based catalysts due to their unique physicochemical properties and large specific surface areas. The edge sites of molybdenum disulfide (MoS_2) are recognized as active centers for the hydrogen evolution reaction [18], but its intrinsic poor conductivity and inert basal plane limit its overall catalytic performance. The combination of gold nanomaterials with MoS_2 has been proven to be an effective strategy for enhancing its HER activity. This is attributed to the superior electronic coupling between MoS_2 and the Au substrate, as well as the abundant edge active sites. First-principles calculations further reveal that an external electric field can effectively modulate the charge transfer and Schottky barrier at the MoS_2/Au interface, even altering its type (from n-type to p-type), and can precisely regulate the adsorption energy of H on the MoS_2 surface [19].

In addition to MOFs and TMDs, Layered Double Hydroxides (LDHs) are also widely used as electrocatalyst supports due to their unique two-dimensional layered structure, tunable metal composition, and stability in alkaline environments. As previously mentioned, loading Au single atoms and Au nanoparticles onto NiFe-LDH can optimize their OER and HER performance, respectively, demonstrating the strong interaction between Au species and the NiFe-LDH support [4]. The layered structure of LDH not only provides stable anchoring sites for Au species, but its own metal sites may also participate in the catalytic process or enhance the activity of Au through interfacial synergistic effects.

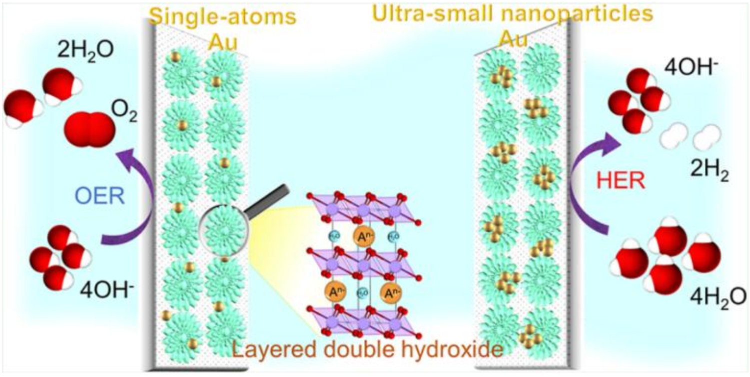

Figure 3. The variation of Au species deposited on NiFe-layered double hydroxide [4]

6. ATOMICALLY PRECISE CONSTRUCTION

Pushing the utilization of gold to its extreme, enabling each gold atom to serve as a catalytic active center, represents another frontier in gold-based catalyst research. The development in this field follows a trajectory from nanoparticles to ultra-small nanoclusters [20], and further to single-atom catalysts (SACs). When the size of metals is reduced to the sub-nanometer scale, their electronic structures exhibit significant quantum size effects, which are markedly different from bulk materials, thereby leading to unique catalytic properties [21]. Atomically precise gold-based catalysts, including single atoms and nanoclusters, not only achieve nearly 100% atomic utilization efficiency but, more importantly, provide structurally uniform and well-defined catalytic active sites. This offers unprecedented opportunities for revealing catalytic reaction mechanisms at the atomic level and establishing clear structure-activity relationships [1].

Single-atom catalysts (SACs) have become a research hotspot in the field of catalysis in recent years [22]. In gold-based single-atom catalysts, individual gold atoms are anchored to specific support materials (such as oxides, layered double hydroxides, and carbon materials) through chemical bonds (e.g., M-O-C, M-N-C), thereby preventing their migration and agglomeration during reactions. This unique structure ensures that each gold atom becomes an isolated, well-defined active center with a clear coordination environment. A study loaded gold single atoms (Au SAs) onto nitrogen-doped carbon (N-doped carbon, NDC) and used it as an electron-regulated substrate, further loading Pt-Ni alloy nanoparticles to form a PtNiNPs/AuSA-NDC composite catalyst [23]. Remarkably, this sophisticated design significantly enhances the catalyst's performance in oxygen reduction reaction (ORR) and hydrogen evolution reaction (HER) in acidic media. In HER, the catalyst exhibits an ultralow overpotential of merely 19.1 mV at a current density of 10 mA cm^{-2}, with its mass activity being 38 times that of commercial Pt/C. Theoretical calculations reveal that the isolated Au single-atom sites can effectively modulate the electronic structure of adjacent Pt-Ni alloy nanoparticles, optimize the adsorption of reaction intermediates, and thereby accelerate the reaction kinetics. In this system, the Au single atoms do not serve as the primary HER active sites but instead act as "electronic promoters," altering the intrinsic catalytic activity of the PtNi alloy through long-range electronic interactions. This reveals a new function of single atoms in catalyst design: in addition to serving as active centers, they can also act as powerful tools for regulating the electronic properties of other active components, achieving synergistic effects. For the HER, the adsorption and recombination of H are critical steps, and the surface of gold nanoparticles may provide a more suitable H adsorption energy. Density functional theory (DFT) calculations also support the potential of single-atom gold as an efficient HER catalyst. Research shows that Au single atoms supported on two-dimensional titanium carbide (TiC_2) (Au-TiC_2) exhibit a theoretical overpotential of -0.17 V, demonstrating promise as an excellent HER electrocatalyst [24].

Gold nanoclusters (Au NCs) are a class of materials that lie between individual atoms and traditional nanoparticles (typically >2 nm), with their size usually ranging from 1 to 2 nm, composed of an exact number of gold atoms and surface ligand molecules [25]. Unlike traditional nanoparticles, whose size and morphology often exhibit a statistical distribution, the atomically precise structure (i.e., the exact three-dimensional arrangement of gold atoms) of many gold nanoclusters can be determined by techniques such as X-ray single-crystal diffraction. This atomic-level precision makes gold nanoclusters ideal model catalysts for understanding catalytic mechanisms and establishing structure-activity relationships at the molecular level [26]. The catalytic performance of gold nanoclusters can be regulated through various methods. First is the size effect, where the number of gold atoms in the cluster directly leads to changes in its electronic structure and HOMO-LUMO energy levels, thereby affecting catalytic activity. Next is the ligand effect. The surface ligands that protect the stability of clusters are not merely inert "protective shells." They can interact with the gold core through electron donor/acceptor effects, thereby influencing the overall electronic properties and catalytic activity of the clusters [27].

7. FUTURE PROSPECTS

Research on gold-based electrocatalysts for the hydrogen evolution reaction (HER) has made remarkable progress over the past decade, completely overturning the traditional view of gold as a catalytically inert metal. Through multi-scale and multi-dimensional structural design and regulation, ranging from macroscopic alloys to atomic-level single atoms and nanoclusters, researchers have systematically enhanced the HER catalytic activity of gold-based materials, enabling them to exhibit performance comparable to or even surpassing that of commercial Pt/C in certain systems [28].

This review summarizes several core research directions in the field and their intrinsic mechanisms [29]. Alloying strategy: By forming binary, ternary, and even high-entropy alloys of gold with metals such as Ru and Pd, or with transition metals such as Fe, Ni, and Co, the adsorption free energy of H* is finely tuned through electronic effects and lattice strain effects, resulting in significant enhancements in catalytic activity and stability. Carrier synergistic effect: By loading gold onto functional carriers such as MOFs, MoS_2, graphene, and LDHs, the electronic properties and local environment of gold sites can be significantly altered through interfacial charge transfer, chemical bonding, and spatial confinement effects, thereby optimizing their catalytic performance [30]. Atomically precise construction: Gold single-atom catalysts and gold nanoclusters with precise atomic numbers push atomic utilization to the limit and provide structurally uniform active sites. These systems are not only highly efficient catalysts but also ideal models for revealing catalytic mechanisms and establishing structure-activity relationships, laying a solid foundation for the rational design of catalysts [8].

Despite significant successes, the further development and commercialization of gold-based HER catalysts still face numerous challenges [31]. Primarily, cost remains a central obstacle. Although strategies such as alloying and single-atomization can substantially reduce the amount of gold used, gold, as a precious metal, has limited reserves and remains expensive. Future research should focus on the concept of using gold as a catalyst to enhance the efficiency of base metals. This involves utilizing a minimal amount of gold as an active additive or structural regulator to activate and optimize catalyst systems primarily composed of earth-abundant elements (such as Fe, Co, Ni, Mo), achieving the best balance between performance and cost. Secondly, stability and durability are key indicators for assessing the practical value of catalysts. Currently, much research on gold-based catalysts emphasizes evaluating initial activity, while studies on their structural evolution and performance degradation mechanisms under high current density, long-term operation (ranging from hundreds to thousands of hours), and complex electrolyte conditions (such as seawater) remain insufficient. Future research should place greater emphasis on the application of operando characterization techniques to monitor the dynamic changes of catalysts in their working state in real time, reveal deactivation mechanisms, and design catalysts with enhanced structural stability and corrosion resistance. Furthermore, scalable synthesis and preparation serve as a bridge connecting laboratory achievements with industrial applications [32]. Many preparation methods for high-performance gold-based catalysts involve complex steps, expensive equipment, or harsh conditions, making large-scale, low-cost, and reproducible production challenging.

Developing simple, green, and scalable synthesis routes, such as the previously mentioned active hydrogen interface reduction strategy [16], is crucial for advancing gold-based catalysts towards practical applications. Finally, a deeper understanding of catalytic mechanisms needs to be strengthened. Although theoretical tools such as DFT calculations, have provided valuable insights, determining the actual reaction pathways and rate-determining steps in complex multi-interface, multi-component catalytic systems remain highly challenging. By integrating advanced computational methods, high spatiotemporal resolution in-situ characterization, and meticulously designed model experiments, in-depth analysis of reaction mechanisms, particularly the detailed processes of proton-coupled electron transfer [33], which will offer clearer guidance for the design of next-generation catalysts.

Looking ahead, research on gold-based electrolytic water hydrogen evolution catalysts will continue to progress towards higher efficiency, greater stability, improved cost-effectiveness, and more clearly understood mechanisms[34]. Emerging research areas, such as the rapid screening and design of catalysts using machine learning and artificial intelligence, the development of integrated electrodes with multifunctional capabilities (e.g., anti-fouling, self-cleaning), and the coupling of HER catalysts with anode oxidation reactions (such as urea oxidation or methanol oxidation) to reduce overall energy consumption, will open new possibilities for the application of gold-based catalysts [35]. Through continuous innovation and in-depth exploration of this ancient metal, we have reason to believe that it will play an indispensable role in the future hydrogen economy, contributing significantly to building a sustainable energy future.

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REFERENCES

[1] X. Zhu, L. Chen, Y. Liu, Z. Tang, Atomically precise Au nanoclusters for electrochemical hydrogen evolution catalysis: Progress and perspectives, Polyoxometalates, 2 (2023) 9140031.

[2] Y. Xu, X. Zhang, Y. Liu, R. Wang, Y. Yang, J. Chen, A critical review of research progress for metal alloy materials in hydrogen evolution and oxygen evolution reaction, Environmental science and pollution research international, 30 (2023) 11302-11320.

[3] Y. Yuan, J. Li, Y. Zhu, Y. Qiao, Z. Kang, Z. Wang, X. Tian, H. Huang, W. Lai, Water in Electrocatalysis, Angew. Chem. Int. Ed., 64 (2025) e202425590.

[4] S. Pattaweepaiboon, P. Samarungkasut, P. Iamprasertkun, P. Arkasalerks, K. Nueangnoraj, A. Boonchun, A. Pumsantier, W. Hirunpinyopas, W. Sirisaksoontorn, Single-Atom to Ultrasmall Au

Nanoparticles Anchored on NiFe Layered Double Hydroxide as Catalyst for Oxygen and Hydrogen Evolution Reactions, ACS Applied Nano Materials, 8 (2024) 438-448.

[5] E. Biehler, Q. Quach, T.M. Abdel-Fattah, Gold Nanoparticle Mesoporous Carbon Composite as Catalyst for Hydrogen Evolution Reaction, Molecules, 29 (2024).

[6] A. Laghrissi, M. Es-Souni, Au-Nanorods Supporting Pd and Pt Nanocatalysts for the Hydrogen Evolution Reaction: Pd Is Revealed to Be a Better Catalyst than Pt, Nanomaterials, 13 (2023).

[7] M. El-Shafie, Hydrogen production by water electrolysis technologies: A review, Results in Engineering, 20 (2023) 101426.

[8] J. Zhu, L. Hu, P. Zhao, L.Y.S. Lee, K.Y. Wong, Recent advances in electrocatalytic hydrogen evolution using nanoparticles, Chemical reviews, 120 (2020) 851-918.

[9] E. Biehler, Q. Quach, T.M. Abdel-Fattah, Gold Nanoparticles AuNP Decorated on Fused Graphene-like Materials for Application in a Hydrogen Generation, Materials, 16 (2023).

[10] D. Deepak, V. Vuruputuri, G. Bhattacharya, J.A. McLaughlin, S.S. Roy, Fabrication of Gold Nanoparticles Embedded Laser-Induced Graphene (LIG) Electrode for Hydrogen Evolution Reaction, C, 9 (2023) 118.

[11] B.H. Alshammari, H. Begum, F.A. Ibrahim, M.S. Hamdy, T.A. Oyshi, N. Khatun, M.A. Hasnat, Electrocatalytic Hydrogen Evolution Reaction from Acetic Acid over Gold Immobilized Glassy Carbon Surface, Catalysts, 13 (2023) 744.

[12] A. Zhu, L. Qiao, K. Liu, G. Gan, C. Luan, D. Lin, Y. Zhou, S. Bu, T. Zhang, K. Liu, T. Song, H. Liu, H. Li, G. Hong, W. Zhang, Rational design of precatalysts and controlled evolution of catalyst-electrolyte interface for efficient hydrogen production, Nat Commun, 16 (2025) 1880.

[13] S. AlAreeqi, C. Ganley, D. Bahamon, K. Polychronopoulou, P. Clancy, L.F. Vega, Rational design of optimal bimetallic and trimetallic nickel-based single-atom alloys for bio-oil upgrading to hydrogen, Nat Commun, 16 (2025) 2639.

[14] T. Kwon, A. Yu, S.-j. Kim, M.H. Kim, C. Lee, Y. Lee, Au-Ru alloy nanofibers as a highly stable and active bifunctional electrocatalyst for acidic water splitting, Applied Surface Science, 563 (2021) 150293.

[15] Z. Li, C. Yu, Y. Kang, X. Zhang, Y. Wen, Z.K. Wang, C. Ma, C. Wang, K. Wang, X. Qu, M. He, Y.W. Zhang, W. Song, Ultra-small hollow ternary alloy nanoparticles for efficient hydrogen evolution reaction, National science review, 8 (2021) nwaa204.

[16] Z. Liu, Y. Jiang, Z. Zhang, X. Wang, K. Liu, Z. Qiao, M. Liu, S. Zhang, Z. Mu, Q. Zhang, C. Gao, Synthesis of noble/non-noble metal alloy nanostructures via an active-hydrogen-involved interfacial reduction strategy, Nature Synthesis, 2 (2023) 119-128.

[17] D.K. Yadav, R. Gupta, V. Ganesan, P.K. Sonkar, M. Yadav, Gold Nanoparticles Incorporated in a Zinc-Based Metal-Organic Framework as Multifunctional Catalyst for the Oxygen Reduction and Hydrogen Evolution Reactions, ChemElectroChem, 5 (2018) 2612-2619.

[18] Jianping Shi, Donglin Ma, G.-F. Han, Directly Grown Monolayer MoS2 on Au Foils As Efficient Hydrogen Evolution Catalysts.

[19] F.L. Ling, T.W. Zhou, X.Q. Liu, W. Kang, W. Zeng, Y.X. Zhang, L. Fang, Y. Lu, M. Zhou, Electric field tuned MoS(2)/metal interface for hydrogen evolution catalyst from first-principles investigations, Nanotechnology, 29 (2018) 03LT01.

[20] Shuai- Peng Chen, Jiajia Zhang, Qi- Xiang Cai, Yubing Si, Ying- Xue Yuan, S.-Q. Zang, Gold clusters assembled homochiralhelical microbowties, SCIENCE ADVANCE S, 11 (2025) eadx9526.

[21] T.D. Tran, M.T.T. Nguyen, H.V. Le, D.N. Nguyen, Q.D. Truong, P.D. Tran, Gold nanoparticle as an outstanding catalyst for the hydrogen evolution reaction, (2018).

[22] N. Cheng, S. Stambula, D. Wang, M.N. Banis, J. Liu, A. Riese, B. Xiao, R. Li, T.K. Sham, L.M. Liu, G.A. Botton, X. Sun, Platinum single-atom and cluster catalysis of the hydrogen evolution reaction, Nat Commun, 7 (2016) 13638.

[23] T.D. Le, D.S. Kim, T.V. Tran, B. Urupalli, G.S. Shin, G.J. Oh, Y.T. Yu, Electronic Structure Engineering of Pt-Ni Alloy NPs by Coupling of Gold Single Atoms on N-Doped Carbon for Highly Efficient Oxygen Reduction Reaction and Hydrogen Evolution Reaction, Small, 20 (2024) e2311971.

[24] H. Guo, S. Gu Kang, S. Geol Lee, First-principles Density Functional Theory Elucidation of the Hydrogen Evolution Reaction on TM-promoted TiC(2) (TM=Fe, Co, Ni, Cu, Ru, Rh, Pd, Ag, Os, Ir, Pt, and Au), Chemphyschem : a European journal of chemical physics and physical chemistry, 24 (2023) e202200823.

[25] Qichen Wang, Yongpeng Lei, Yuchao Wang, Yi Liu, Chengye Song, Jian Zeng, Yaohao Song, Xidong Duan, Dingsheng Wang, Y. Li, Atomic-scale engineering of chemical vapor deposition-grown 2D transition metal dichalcogenides for electrocatalysis, Energ Environ Sci, 13 (2020) 1593-1616.

[26] Q. Quan, Y. Zhang, H. Li, W. Wang, P. Xie, D. Chen, W. Wang, Y. Meng, D. Yin, Y. Li, D. Song, L. Chen, S. Li, C. Yang, T. Yanagida, C.Y. Wong, S. Yip, J.C. Ho, Atomic-scale self-rearrangement of hetero-metastable phases into high-density single-atom catalysts for the oxygen evolution reaction, Nat Commun, 16 (2025) 2908.

[27] T. Kawawaki, Y. Negishi, Gold Nanoclusters as Electrocatalysts for Energy Conversion, Nanomaterials, 10 (2020).

[28] S. Guan, Y. Liu, H. Zhang, R. Shen, H. Wen, N. Kang, J. Zhou, B. Liu, Y. Fan, J. Jiang, B. Li, Recent Advances and Perspectives on Supported Catalysts for Heterogeneous Hydrogen Production from Ammonia Borane, Adv Sci (Weinh), 10 (2023) e2300726.

[29] T. Tabakova, Recent Advances in Design of Gold-Based Catalysts for H2 Clean-Up Reactions, Front Chem, 7 (2019) 517.

[30] Y. Sun, Y. Zang, B. He, G. Lin, Z. Liu, L. Yang, L. Chen, L. Li, X. Liu, C. Shen, H. Qiu, Soft nanoforest of metal single atoms for free diffusion catalysis, Sci Adv, 11 (2025) eadq2948.

[31] X. Chen, X.T. Wang, J.B. Le, S.M. Li, X. Wang, Y.J. Zhang, P. Radjenovic, Y. Zhao, Y.H. Wang, X.M. Lin, J.C. Dong, J.F. Li, Revealing the role of interfacial water and key intermediates at ruthenium surfaces in the alkaline hydrogen evolution reaction, Nat Commun, 14 (2023) 5289.

[32] M.A. Qadeer, X. Zhang, M.A. Farid, M. Tanveer, Y. Yan, S. Du, Z.-F. Huang, M. Tahir, J.-J. Zou, A review on fundamentals for designing hydrogen evolution electrocatalyst, Journal of Power Sources, 613 (2024) 234856.

[33] J. Huang, R. Wang, H. Sheng, X. Zhu, R. Dominic Ross, D. Hua, L. Lin, Y. Li, Q. Zhang, L. Gu, X. Wang, P. Xu, J. Lu, S. Jiang, J. Han, B. Song, S. Jin, Isotope-dependent Tafel analysis probes proton transfer kinetics during electrocatalytic water splitting, Nature chemistry, (2025).

[34] P. Anand, S. Kumar, M. Birare, C.-H. Tsai, S.-H. Ding, Y.-P. Fu, Ru-CuO/NiMn-LDH heterostructured electrocatalyst for urea oxidation and hydrogen evolution reactions, Journal of Alloys and Compounds, 1032 (2025) 181208.

[35] S. Ke, R. Mi, X. Min, X. Zhu, C. Wu, X. Li, B. Yang, X. Wu, Y. Liu, Z. Huang, M. Fang, Strong-weak dual interface engineered electrocatalyst for large current density hydrogen evolution reaction, Communications Materials, 6 (2025).