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Review

Sustainable synthesis of supported metal nanocatalysts for electrochemical hydrogen evolution

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ABSTRACT

Among the various types of heterogeneous catalysts, supported metal nanocatalysts (SMNCs) have attracted widespread interest in chemistry and materials science, due to their advantageous features, such as high efficiency, stability, and reusability for catalytic reactions. However, to obtain well-defined SMNCs and inhibit nanoparticle aggregation, traditional approaches generally involve numerous organic reagents, complex steps, and specialized equipment, thus hindering the practical and large-scale synthesis of SMNCs. In this review, we summarize green and sustainable synthetic methodologies for the assembly of SMNCs, including low temperature pyrolysis and solid-state, surfactant- and reductant-free, and ionic liquid assisted syntheses. The conventional application of SMNCs for electrochemical hydrogen evolution and the corresponding achievements are subsequently discussed. Finally, future perspectives toward the sustainable production of SMNCs are presented.

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1. Introduction

With the ongoing energy crisis and environmental pollution increasing in severity, the field of catalysis is being extensively researched and rapidly developed. Catalysis is an important methodology in green chemistry, which entails chemical processes that generate lower amounts of pollutants and enable syntheses that utilize sustainable resources for the production of desired products [1–6]. Generally, the performance of catalytic systems is intricately related to the choice of catalyst and their structures and properties, which are highly diverse. Sup-

ported metal nanocatalysts (SMNCs), which are heterogeneous catalysts, have several significant advantages [7–9]. Firstly, metal nanoparticles (NPs) loaded on a support can markedly decrease the surface energy, thus limiting NP aggregation and extending catalyst service life [10]. Secondly, the support improves metal NP dispersion and enhances catalytic activity through an efficient synergistic and electronic effect between metal NPs and the support. Finally, compared to naked metal nanocatalysts, SMNCs can be readily recovered without the necessity of tedious and expensive separation processes (Fig. 1(a)) [11–14]. In view of these merits, the objective of fabricat-

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Fig. 1. (a) Advantages of SMNCs and (b) conventional and (c) sustainable synthetic strategies for SMNCs.

ing and applying various SMNCs has garnered substantial research interests globally.

In recent decades, considerable efforts have been devoted to enhancing catalytic performance of SMNCs by modulating and optimizing their size, shape, composition and structure, among other parameters [15–20]. Accordingly, various SMNCs have been developed *via* numerous traditional methods, such as precipitation [21–27], sol-gel [28–32], solvothermal [33–38], and high temperature pyrolysis [39–44] (Fig. 1(b)). However, as these methods commonly suffer the disadvantages of requiring organic reagents, complex synthetic steps, or special equipment, they do not conform to the concept of green and sustainable synthesis [45]. Consequently, straightforward and highly efficient methods for the preparation of metal NPs with clean surfaces and ultrafine sizes, which are uniformly dispersed on supports are highly desirable. Moreover, a reduction in the use and generation of harmful substances during catalyst preparation, as well as during application would be highly beneficial [46].

With this consideration, a number of efficient synthetic strategies have been employed for the production of SMNCs, including solid-state synthesis [47–50], low temperature pyrolysis [51,52], surfactant- and reductant-free synthesis [53,54], and ionic liquid (IL) assisted synthesis [55] (Fig. 1(c)). These synthetic approaches provide eco-friendly routes that conform to the requirements of green chemistry. They have several advantages over traditional synthetic techniques, as listed below (Fig. 2):

(1) Simplified synthetic procedure: The majority of these techniques do not require surfactants, capped reagents, and post-process steps for cleaning the catalyst surface. Additionally, several techniques do not involve solvents, which renders them more convenient.

(2) Eco-friendly synthesis: These synthetic approaches avoid the use of excessively large volumes of organic reagents (e.g., surfactant, solvent, etc.), which are generally harmful for the ecosystem.

(3) High atom economy: In the majority of cases, precursor

Fig. 2. Advantages of sustainable methods for the generation of SMNCs.

components are fully transformed into products, exhibiting a high atom economy. These features ensure high-efficiency and low-cost.

(4) Low amounts of by-products: Simplified synthetic procedures and a high atom economy ensure excellent product selectivity, generating minimal by-products.

These unique features are beneficial for the sustainable development of highly efficient SMNCs, as well as for their scalable applications. In this review, major advancements for the preparation of SMNCs by the above-mentioned sustainable synthetic methodologies are outlined, with emphasis on their featured advantages, preparation conditions, material characteristics, and synthetic mechanisms. In addition, the typical application of SMNCs for the electrochemical hydrogen evolution reaction (HER) and the corresponding achievements are discussed. In the final section of this review, the challenges and prospective directions concerning the sustainable production of SMNCs are proposed.

2. Sustainable synthesis of SMNCs

2.1. Solid-state synthesis

Solid-state synthesis is concerned with the chemical and physical changes in solids, and is utilized for the production of novel materials, thus simplifying complex processes by employing grinding or ball milling. These operations are ordinarily performed on a hard surface in the absence of liquids, however, for a number of specific reactions, the addition of a small amount of liquid is necessary, as it induces and/or significantly accelerates reactions between solids [56]. Although various materials have been dedicatedly developed over the years by solid-state synthesis, its reaction mechanisms remain debatable and currently, the most widely accepted mechanisms are the hot spot theory, and the magma-plasma model. Hot spot theory was proposed by considering frictional processes between two solid surfaces, where the local temperature would raise to above 1000 °C for short periods (10^{-3} – 10^{-4} s) [57]. The magma-plasma (or transient-plasma) model was originally developed by considering direct influences. This model generally applies to solid reactions taking place at the impact points, and is associated with a high local temperature (10^4 °C) and

ejection of energetic species. Considering the advantages of straightforward operation and short reaction times, this strategy provides an attractive alternative to traditional solvent-based routes for the synthesis of SMNCs [58–60]. Based on the various methodologies, solid-state synthesis can be divided into two categories: mortar-pestle milling, and ball milling, which have been used to produce numerous SMNCs (Table 1).

Table 1

Summary of SMNCs assembled by sustainable synthetic approaches.

Catalysts	Methods	Key factors for catalytic applications	Ref.
Ru nanoparticles	a	Size	[48]
Ag NPs/MWCNT	a	Size/loading	[61]
Pt(0), Ir(0), and Pt(0)-Ir(0) alloy NPs	a	Size	[63]
Ru(0) and PPH composites	a	Size	[64]
Au cluster	a	Size	[66]
M NP/C, M = Rh, Ru, Ir	a	Size	[67]
Ru@GnP	b	Crystal faces/size	[68]
Pd/SWCNT	b	Size	[70]
Fe@MG-CO ₂	b	Substrate	[74]
Aluminum/iron Oxide/graphite mixture	b	Synergistic effect	[76]
Au, Ag, Cu, Ni, Pd, Pt, Cu ₃ Au NPs	a	Size	[77]
Pd/CeO ₂	b	Size/interface	[78]
Au/SiO ₂ and Au/Al ₂ O ₃	c	Size	[47]
Ru/C	c	Size	[79]
Pt-Ni alloy nanoparticles	c	Size/synergistic effect	[80]
Mn-Co oxide/NCNT	c	N-doped/synergistic effect	[81]
M NPs/BNNS (M = Au, Au-Ni, Au-Co, Au-Cu)	c	Crystal faces /synergistic effect	[82]
GNS-RuNPs	c	Size	[84]
Pd/HAP	c	Size	[85]
M/SWNT (M = Au, Pt)	d	Size	[92]
M cluster/rGO (M = Au, Pt, Pd)	d	Size	[93]
Pd/GO	d	Size	[94]
Pd NP@N-CNTs	d	Size	[97]
M NPs/PC (M = Ir, Rh, and Ru)	d	Size/loading	[98]
Pd/GDYO	d	Size/substrate	[101]
M NPs/graphite (M = Au, Pd, Ag, Ni, and Fe)	d	Metal species	[109]
MXene/Ag	d	Size	[110]
M NPs/CDG (Ru, Rh)	e	Size and IL layer	[113]
PtNi NPs/C	e	Size and IL layer	[121]
SnSe/CN	b	Quantum-dots	[122]
Cu/Cr ₂ O ₃	b	Size	[123]
Ag/WO _{2.9} /g-C ₃ N ₄	b	Size/cocatalyst	[124]
Co ₉ S ₈ /C	b	Size/heteroatoms	[125]
CoFe ₂ O ₄ -RGO	b	Synergistic effect	[126]
Ni-rGO	b	Size	[127]
WO ₃ /TiO ₂	b	Loading/interface	[128]
SnO ₂ /TiO ₂	b	Loading/interface	[129]
Cu-Mn/HT	b	Size/synergistic effect	[130]

(To be continued)

Table 1 (continued)

Catalysts	Methods	Key factors for catalytic applications	Ref.
RuHSAG-TPA	b	Size/synergistic effect	[131]
Cu/Al ₂ O ₃	b	Synergistic effect	[132]
Ag/Al ₂ O ₃	b	Metal valence state	[133]
Mn/TiO ₂	c	Loading/crystallinity	[134]
CuO-TiO ₂	c	Loading/synergistic effect	[135]
V/CeO ₂	c	Size	[136]
Co/C	c	Size	[137]
Ni/M _x O-ZrO ₂	c	Oxygen doping	[138]
Ru/TiO ₂	c	Metal species	[139]
Pd/CeO ₂	c	Size/synergetic effect	[140]
Fe-N-C	c	Interface	[141]
Rh/CeO ₂	c	Size	[142]
Cu-doped C ₃ N ₄	c	Metal valence state	[143]
Ni/Al ₂ O ₃	d	Size	[144]
Ag/MWCNTs	d	Size	[145]
Pd-Ag/G	d	Size	[146]
Au/SiO ₂	d	Size/interface	[147]
TiO ₂ /metal (Au, Ag, Fe)	d	Size	[148]
Cu/SWCNT	d	Size	[149]
Cu@C ₃ N ₄	d	Metal resources	[150]
Ag-Pd/TiO ₂	d	Loading/synergistic effect	[151]
3Au1Sn/ZnO	e	Size/synergistic effect	[152]
Nb/TiO ₂	e	Size/loading	[153]
CuS-OEs/rGO	e	Morphology	[154]
Ag-CeO ₂	e	Size	[155]
FeP _{MBMG} /CNT	e	Loading/IL species	[156]
PtCu/rGO	e	Morphology	[157]
Pt/MWCNTs	e	Size	[158]
Pd-SiO ₂	e	Size/loading	[159]
AuPt alloy/rGO	e	Size/synergistic effect	[160]

a: Mortar-pestle milling; b: Ball milling; c: Low temperature pyrolysis; d: Surfactant- and reductant-free synthesis; e: Ionic liquid-assisted synthesis.

Mortar-pestle milling. The original implementation of this method was in foodstuffs production, and it was then extended to various other materials (e.g., paints, medicines). Moreover, it is commonly practiced in laboratories to decrease material size or mix samples, while it has been very rarely implemented for the synthesis of SMNCs. Mortar-pestle milling can effectively ameliorate challenges associated with traditional solution-based approaches, such as harsh reaction conditions, complex operations, and expensive equipment, among others [49,61,62]. After several years of development, a variety of SMNCs (based on Ru, Pt, Ir, etc.) with controlled NP sizes and surface states have been successfully synthesized by mortar-pestle milling [48,63–65]. For instance, Wang's group [66] applied a milling-mediated solid-state reduction method to delicately synthesize Au clusters on a surface-functionalized support. In their synthesis, the Au precursor was reduced in situ by NaBH₄ at the solid support surface, and the size of the produced Au NPs in a fine dispersion was measured to be 1.0 nm. Additionally, it was discovered that the NP size could be readily modified by simply changing the load capacity of Au.

Very recently, our group [67] used the mortar-pestle milling

method to successfully assemble several types of noble metal NPs on various carbon matrixes (M NP/C, M = Rh, Ru, Ir) (Fig. 3(a), Table 1). In a typical synthesis, the metal precursor, sodium hydroxide, sodium borohydride, and the carbon support were blended uniformly and the reduction of the precursor occurred during continuous milling of the mixture. It has been proposed that sodium hydroxide (NaOH) and the carbon support play key roles in determining both the size and dispersion of NPs, whereby OH⁻ coordinated with the metal precursor forms an M–OH intermediate and slows down the reduction rate toward small metal NPs; whereas carbon substrates markedly decrease the surface energy and efficiently limit the aggregation of metal NPs, to achieve their high dispersion. The resultant metal NPs, with a clean catalytic surface and small size were extensively distributed on the carbon matrix, as demonstrated by TEM characterization. As shown in Figs. 3(b)–(g), the sizes of Rh, Ru, and Ir NPs were 1.87, 2.05, and 3.17 nm, respectively. It should be noted that the NP size was related to the standard reduction potentials, thus the Ir NP/C delivered the largest size due to the redox potential of Ir/Ir³⁺ being the highest. As organic reagents and the pretreatment of matrixes were not involved in the synthesis, the large-scale production of such SMNCs could be readily achieved via this strategy.

Ball milling. Compared to mortar-pestle milling, ball milling is simpler to scale up, which can broaden the application scope. The most significant difference between ball, and mortar-pestle milling is that the former is often performed in an airtight container filled with a suitable gas, which endows the final NPs with a controllable surface [68–72]. A number of elaborate strategies based on ball-mixing have been successfully proposed in recent years [61,73–77]. For example, Li and co-workers [68] reported a ball-milling-assisted method for the preparation of uniformly dispersive Ru NPs on edge-carboxylic acid-functionalized graphene nanoplatelets (Ru@GnP) (Table 1). It was demonstrated that ball-milling of graphite with dry

ice enabled the formation of abundant carboxylic acid radicals on the edge of CGnP, which could enhance the loading of Ru ions, and thus control the NP size. As shown in Figs. 4(a) and (b), the copious produced Ru NPs were ultrafine, with an average size less than 2 nm, which ensures abundant highly active sites on Ru@GnP, toward excellent HER activities in acidic and alkaline solutions. In addition to the synthesis of carbon-supported metal NPs, the ball milling method is useful for the synthesis of metal oxide-loaded metal NPs. As a representative example, Trovarelli et al. [78] developed a controlled ball milling procedure to produce a Pd/CeO₂ nanocomposite using Pd NPs (less than 2 nm in size) as precursors instead of the common metal precursor (Table 1). Notably, a unique Pd–O–Ce interface was achieved under ball milling, due to the uniform coverage of Pd NPs on the CeO₂ surface. It was surmised that the relatively close contact at nano-scale, accompanying the mechanical power generated in the mixing process, enhanced the redox exchange between Pd and CeO₂, which is favorable for creating abundant active and stable sites composed of PdO_x dissolved into the surface layer of CeO₂.

Based on the above-discussed factors, it is evident that solid-state synthesis presents a viable alternative for the production of SMNCs. Advantageous features include improved efficiency with regard to time, atom transformation and energy usage, as well as the possibility of discovering novel products and enhanced catalytic performance. Therefore, the application of this approach is likely to continue to increase. It is important to note, however, that this method suffers from certain challenges and limitations with regards to the scalable production of diverse SMNCs. Firstly, the distribution of metal NPs in SMNCs is ordinarily not uniform in solid-state synthesis, which results from the inadequate dispersion of the metal precursor and carbon matrix, as well as the rapid reaction rate. Secondly, it is not possible to efficiently control the surface state of metal NPs, due to the rapid reaction rate and because the majority of solid syntheses are performed in air. Thirdly, it does not lend itself to observing reaction processes or/and materials and the associated reaction mechanisms at microscopic or molecular levels. Finally, the scope of metals and carbon matrixes remains limited, which would restrict the implementation of this strategy for generating widely applicable SMNCs. Overall, if these drawbacks can be overcome, this approach could be a viable alternative route for the synthesis of various SMNCs.

Fig. 3. (a) Schematic illustration of M (Rh, Ru, Ir) NP/C production; TEM and HRTEM images of Rh NP/C (b,e), Ru NP/C (c,f), and Ir NP/C (d,g). Reprinted with permission from Ref. [67]. Copyright 2018, Wiley-VCH.

Fig. 4. TEM images of Ru@GnP before (a) and after (b) heat treatment. Reprinted with permission from Ref. [68]. Copyright 2018, Wiley-VCH.

2.2. Low temperature pyrolysis

Synthesis *via* pyrolysis, especially under high temperatures, is among the most commonly practiced strategies for the production of SMNCs. Due to a high surface energy, however, the newly produced metal NPs tend to aggregate and gradually enlarge, resulting in their increased size and uneven distribution. In addition to target products, large amounts of byproducts are generated *via* high temperature pyrolysis, as side reactions occur readily and are accelerated by high temperatures. Additionally, high temperature pyrolysis generates large volumes of hazardous gases (e.g., CO, CO₂) and requires substantial energy inputs, as well as lengthy synthesis times. Therefore, the ability to decrease synthesis temperatures, in order to abate and even eliminate the above-mentioned disadvantages toward well-designed SMNCs, is of considerable importance. Compared to high temperature pyrolysis, low temperature pyrolysis presents a more convenient, economical, and efficient method. Importantly, metal NPs of target products are controllable, presenting small sizes and adequate distribution, as well as a fine surface state. After several years of development, diversiform SMNCs (Table 1) have been successfully synthesized *via* this strategy by the simple pyrolysis of metal precursor and support mixtures at low temperatures [47,79–83].

As a representative example of low temperature pyrolysis, Xu et al. [79] have employed this approach for the successful production of supported Ru NPs by using Ru₃(CO)₁₂ as the metal precursor, and conductive carbon as the matrix (Table 1); Ru₃(CO)₁₂ was adsorbed on the surface of the carbon matrix and then transformed in situ to Ru NPs at a low temperature (300 °C). TEM images indicated that monodispersed Ru NPs of Ru/C-300 with a size of 1.48 nm were homogeneously dispersed on the carbon matrix (Figs. 5(a) and (b)). Benefiting from this feature, Ru/C-300 exhibited excellent catalytic activities for the electrochemical HER, as well as ammonia borane hydrolysis. Moreover, metal acetylacetonate precursors can be utilized to synthesize SMNCs by low temperature pyrolysis. Kim et al. [84] discovered that the Ru(acac)₃ precursor thermally decomposed to metallic Ru NPs at 300 °C (Table 1). The resultant ultrafine Ru NPs with a size of 1.7 nm were uniformly distributed on the surface of graphene nanosheets (GNSs). Increasing the pyrolysis temperature from 300 to 350 °C, resulted in a notable increase in Ru size, from 1.7 to 15 nm, and was

Fig. 5. (a) TEM and HRTEM images of Ru/C-300; (b) Corresponding NP size distribution. Reprinted with permission from Ref. [79]. Copyright 2018, The Royal Society of Chemistry.

accompanied by inadequate NP distribution. This suggests that the pyrolysis temperature of this system is crucial for delivering Ru NPs in an ultrafine size and with good dispersion. Very recently, Guo et al. [85] successfully fabricated uniform ultrafine Pd NPs with excellent dispersion on hydroxyapatite (HAP) *via* this strategy, using Pd(acac)₂ as the precursor (Table 1). Interestingly, during the synthesis, Pd(acac)₂ was initially transformed to the liquid phase at 120 °C, owing to its low melting point (116 °C), and then distributed on the HAP surface to generate a thermodynamically stable monolayer. After annealing by hydrogen under the same temperature, Pd NPs were obtained on the HAP surface with a size of 1.2 nm, which is smaller than that of Pd NPs (10 nm), achieved by the traditional wet impregnation strategy (Figs. 6(a)–(d)), demonstrating the advantages of low temperature pyrolysis. It was remarkable that the reduction conditions played an important role in the synthesis of such highly dispersive and ultrafine Pd NPs. ^a1Pd/HAP-SSD with small and abundant Pd NPs exhibited an excellent catalytic performance in the hydrogenation of phenol to cyclohexanone. However, it should be noted that this strategy necessitates an additional reduction process, which diminishes its convenience and economic value to a degree.

Although low temperature pyrolysis is considered as a suitable route for producing well-designed SMNCs, in some cases, aggregation of metal NPs still occurs and results in a significant loss in activity, suggesting that this strategy does present limitations. Presently, only the use of metal complexes (e.g., Ru₃(CO)₁₂, Pd(acac)₂) as reaction precursors can achieve well-defined SMNCs. Hence, the exploration of a wider variety of metal precursors with low-cost and environment-friendly features is anticipated. Moreover, ordinary temperature control procedures prohibit the development of various SMNCs via this strategy, which motivates researchers to develop unique control procedures for each sample. Advancements concerning the two above-mentioned factors, would generate additional interest for the production of SMNCs *via* low temperature pyrolysis.

Fig. 6. TEM images of ^a1Pd/HAP-SSD (a), ^b1Pd/HAP-SSD (c), and 1Pd/HAP-WI (d); (b) HAADF-STEM image of ^a1Pd/HAP-SSD. Reprinted with permission from Ref. [85]. Copyright 2017, The Royal Society of Chemistry.

ysis.

2.3. Surfactant- and reductant-free synthesis

With the elimination of organic reagents and chemical reductants, surfactant- and reductant-free synthesis of SMNCs, especially in aqueous solution, can effectively overcome a number of drawbacks of traditional solution-based methods [86–91]. The driving force behind this method is the spontaneous redox reaction between the precursor and matrix (electroless deposition), where the matrix acts as both the reductant and stabilizer. Currently, carbon-based materials with superior conductivity are widely applied as matrixes for the synthesis of SMNCs, due to their relatively low redox potentials compared to those of other supports.

In recent years, various SMNCs based on Pt, Au, Ag, and Pd have been successfully assembled *via* this strategy [92–100]. For example, Mao et al. [101] synthesized ultrasmall Pd NPs supported on graphdiyne (GDY) or graphdiyne oxide (GDYO) by exploiting the lower redox potential of the supports compared to that of PdCl_4^{2-} (Table 1). The reduction potentials of GDY, GDYO and PdCl_4^{2-} are –0.33, –0.21 and 0.62 V, respectively, as shown in Fig. 7(a), as calculated by equations: $\Phi = h\nu - E_{\text{Fermi}} + E_{\text{cutoff}}$ and $\Phi/e = E(\text{vs. SHE}) + 4.44$ V, where Φ is the work function; $h\nu$ and E_{Fermi} are the photo energy of the excitation light and Fermi level edge, respectively. The E_{cutoff} value can be obtained by UPS measurements [102–104]. The results revealed that PdCl_4^{2-} could be extensively reduced by GDY and GDYO, without additional reductants. In this case, the GDY and GDYO supports served as not only as reductants, but also as stabilizers for the formation of ultrafine Pd NPs. They proposed that the surface oxidation of GDY to GDYO would introduce more oxygen-containing functional groups, which was beneficial for stabilizing GDYO in aqueous solution, and more im-

portantly, facilitating the immobilization of Pd NPs on the GDYO surface and preventing Pd NPs from enlarging. Thus, the as-synthesized Pd NPs exhibited a diameter of 1.3 nm in a narrow size distribution, as illustrated in Figs. 7(b), (c). The surfactant-free and highly-dispersed Pd cluster supported on the surface of unique GDYO, Pd/GDYO exhibited outstanding catalytic activity for the reduction of 4-nitrophenol with NaBH_4 [105–107]. The ability to utilize substrates as both the reductant and stabilizer is an effective approach for the design and development of carbon-supported Pd NPs, however, the catalyst metal content is difficult to control in this case.

Moreover, the relatively high redox potential of GDYO hinders its application for the synthesis of a wider range of metal NPs via this strategy. Recently, our group developed a new type of carbon matrix, namely porous carbon (PC), with a redox potential of –0.27 V, which is lower than that of GDYO (–0.21 V), CNTs (0.50 V) [108], and GO (0.72 V) (Figs. 8(a) and (b)) [98]. This factor enables the PC to deposit various metal NPs, previously unexplored for this method. As expected, several platinum group metal NPs (PGM = Ir, Rh, and Ru) with a super-small size, good dispersion, and a fine uniformity were successfully achieved using PC as the support, at room temperature, without the addition of organic reagents or reductants (Table 1). Ir, Rh, and Ru NPs with a size of 0.96, 1.11, and 1.37 nm, respectively, can be clearly observed in Figs. 8(c)–(e). Additionally, it was established that both NP size and metal content were readily controllable by the deposition temperature. Although diverse oxygen-containing groups were present on the surface of PC, a series of studies discovered that only –CHO and –C–OH were acting as the reducing reagents for the deposition of metal NPs. When applied, the developed SMNCs exhibited excellent HER performance in both acidic and alkaline media. Overall, this work provides a new support for surfactant- and reductant-free (electroless deposition) synthesis of various metal NPs.

Furthermore, Pandey et al. studied the influence of surface states (e.g., defects, hydroxyl function groups) of the carbon material on its redox ability for the surfactant- and reduct-

Fig. 7. (a) Schematic illustration of Pd/GDYO production; TEM images of Pd/GDY (b) and Pd/GDYO (c). Reprinted with permission from Ref. [101]. Copyright 2015, American Chemical Society.

Fig. 8. UPS spectrum (a) and schematic illustration (b) of redox potentials for PC and PGMs; TEM images of Ir NP/PC (c), Rh NP/PC (d), and Ru NP/PC (e). Reprinted with permission from Ref. [98]. Copyright 2019, Wiley-VCH.

ant-free (electroless deposition) synthesis of metal NPs [109]. In their study, a series of chemical and mechanical treatments (e.g., surface scratching, oxygen plasma treatment, or immersion in acid) were adopted to dispose the graphite, yielding several graphite samples with various surface states. After careful analysis, it was found that the number of corresponding surface defects increased according to the following sequence: acid treated graphite > scratched graphite > normal graphite (untreated graphite) > HOPG. All graphite samples were capable of noble metal deposition (e.g. Pd, Au and Pt) (Fig. 9(a)). Interestingly, when the graphite was treated with oxygen plasma, it became enriched with oxygen-containing functionalized defects, which imparted it with strong redox ability for electroless deposition of non-noble metal NPs (Fe and Ni) (Fig. 9(b)).

Additionally, Peng et al. [110] employed this method to successfully develop a novel MXene/Ag composite *via* a spontaneous redox reaction between Ag (I) and surface Ti (III) of MXene (Table 1, Figs. 10(a)–(d)). During the reaction process, the original Ti (III) was converted to the terminated high-valence Ti (IV) species, accompanied by the reduction of Ag (I) to metal Ag NPs. Thus, the high propensity for Ag ion self-reduction was ascribed to the low redox potential of the activated low-valence Ti species. It was additionally established that the size of Ag NPs could be readily modulated by varying the initial concentration of Ag ions. It should be noted that the layered structure of MXene further stabilizes the metal NPs and restricts their aggregation [111,112]. However, the resultant size of Ag NPs in this case was relatively large, implying that the application of the MXene matrix in this system did not adequately control the size of Ag NPs.

In the absence of surfactants and reductants, metal deposition occurs only when the redox potential of the metal precursor is higher than that of the support. Despite this advancement, it should be noted that surfactant- and reductant-free (electroless deposition) synthesis is not a versatile strategy for the production of diverse SMNCs. Presently, only noble metal-based (Pt, Au, Ag, Pd, Ir, Rh, Ru, Fe, and Ni) NP-containing SMNCs can be successfully synthesized by this strategy (Table 1). Therefore, further research concerning the development of diverse matrixes for the generation of a wider range of SMNCs

Fig. 9. (a) Synthetic scheme of metal deposition; (b) Photos of various samples. Reprinted with permission from Ref. [109]. Copyright 2012, American Chemical Society.

Fig. 10. SEM (a), TEM (b), and HRTEM (c, d) images of MXene/Ag. Reprinted with permission from Ref. [110]. Copyright 2016, American Chemical Society.

is necessary.

2.4. Ionic liquid-assisted synthesis

After several years of development, significant achievements have been realized toward the utilization of ILs as green and sustainable solvents for the production of SMNCs. Ordinarily, ILs are ionic salts that exist in the liquid state at room temperature, and are typically composed of organic N-containing heterocyclic cations and inorganic anions. ILs possess numerous merits, including reduced volatility, non-toxicity, a low vapor pressure, and high physico-chemical stability, which render them ideal candidates for the substitution of traditional volatile organic solvents and the sustainable synthesis of SMNCs [113–116]. It has been reported that the use of ILs as reaction media is highly efficient for the controllable synthesis of metal NPs of SMNCs, presenting several benefits [117–120]: (1) the adjustable miscibility of ILs ensures facile recycling of the solvent and effective stabilization of metal NPs; (2) ILs promote syntheses with highly polar precursors under ambient, as well as non-aqueous conditions; (3) ILs can be arranged on the metal surface, which promotes the selective formation of surface-attached anions, thereby controlling the size of metal NPs and preventing their agglomeration. These features enable the generation of metal NPs of SMNCs with controllable surface states and sizes and adequate stability.

Recently, Janiak et al. [113] discovered that the IL assistance route can be implemented to successfully synthesize well-defined carbon-supported Rh and Ru materials. In their synthesis, $\text{Ru}_3(\text{CO})_{12}/\text{Rh}_6(\text{CO})_{16}$ and graphene acted as metal sources and the substrate, respectively (Table 1). Graphene presented stable single-layer flake morphology only under the assistance of BMImBF_4 , and the obtained metal (Rh, Ru) NPs exhibited ultrafine sizes and good dispersion, as demonstrated by TEM observations. As shown in Figs. 11(a)–(d), both Ru and Rh NPs were well deposited on graphene with sizes of 2.2 and

Fig. 11. TEM and SAED images of Ru (a,b) and Rh-NP (c,d) supported on CDG. Reprinted with permission from Ref. [113]. Copyright 2011, Elsevier.

2.8 nm, respectively. Moreover, the use of ILs delivered highly stable carbon-supported Rh and Ru NPs for cyclohexene hydrogenation. After 10 runs, the size of Ru and Rh NPs (2.7 nm for Ru, 2.8 nm for Rh) had increased marginally compared to that of the initial samples. ILs have been employed for the deposition of Ru NPs on the surface of Na-based montmorillonite (Na-MMT). Following treatment with the [TMG][TFA] IL, the surface Na cations were exchanged with TMG (TMG-MMT). This species coordinates with the metal precursors to decrease the deposition rate of metal NPs, assuring the assembly of small-sized, highly dispersed metal NPs. Benefiting from the unique features of the IL-assisted strategy, the obtained Ru/MMT sample displayed an excellent activity for the hydrogenation of benzene, superior to traditional Ru/C and Ru/Al₂O₃ catalysts. Furthermore, Choi et al. [121] established that the [BMIM][TF₂N] IL was beneficial for the synthesis of bimetallic PtNi NPs, resulting in their small size (2–4 nm) and high degree of dispersion on the support (Figs. 12(a)–(e), Table 1), and consequently, their superior catalytic performance.

The above-discussed results clearly illustrate that ILs can effectively maintain a stable reaction environment and enable fine tuning of the size and dispersion of metal NPs, as well as their surface state, to deliver highly active and stable SMNCs (Table 1). Although considerable achievements have been realized in the synthesis of SMNCs via IL-assisted methods, there is still room for improvement of the synthetic procedure, as well as the catalytic applications of SMNCs. Firstly, low-cost, non-toxic, and environment-friendly ILs should be utilized in the majority of cases. Secondly, the development of well-designed SMNCs should provide information on the kinetics and mechanisms of metal NP formation by in situ (or operando) means. Finally, diversification regarding the types of metal precursors and matrixes for the production of varied

Fig. 12. (a-d) TEM images of PtNi-alloy/C; (e) Corresponding alloy NP size distribution. Reprinted with permission from Ref. [121]. Copyright 2017, Elsevier.

SMNCs is highly anticipated. Consequently, SMNCs targeted via this strategy could be readily achieved by considering the above-mentioned points.

3. Design considerations of SMNCs

As SMNCs are typically heterogeneous catalysts, their design should adhere to the key principles of synergistic design, considering intrinsic active sites, mass transfer, and electron transportation, as well as mechanical and chemical durability and recyclability of the catalyst, aiming at cost-effective, high-efficiency, and environmentally friendly syntheses and applications. (Fig. 13). (1) NP surface state modulation. To achieve excellent SMNC activity, the intrinsic activity of the active components (NPs) needs to be high, which is usually determined by their surface state, as it markedly affects the ability for ad-/de-sorption of active intermediates, thus, controlling NP intrinsic activity [161–168]. Generally, the surface state of NPs is strongly related to their coordination environment and the interactions between NPs and the support. Therefore, modulating the coordination environment and adjusting NP-support interactions is crucial for achieving NPs with high intrinsic activity. (2) Synergistic NP surface state and crystalline facet modulation. It is well known that the intrinsic activity of NPs can be significantly affected by the crystalline

Fig. 13. Design considerations of SMNCs.

facet effect [169–179]. The low-coordination plane of NPs generally contains a high density of atomic steps/kinks, which provide copious active sites, whereas the high-index plane of NPs generally exhibits high intrinsic activity. Therefore, coupling this effect with NP surface state modulation would significantly enhance the catalytic activity of SMNCs. (3) Synergistic co-catalyst (or heterojunction) construction. Heterogeneous catalytic reactions ordinarily include several elementary reaction steps. Each one may require a specific active site and generally, a single active component doesn't satisfy the demand of high efficiency and selectivity. To achieve adequate catalytic activity, a co-component or heterojunction can be introduced, in order to jointly catalyze the reaction and balance intermediates and elementary steps. Moreover, the additional co-catalyst (or heterojunction) may modify the surface state of the natural active component, thus, enhancing its intrinsic activity [180–188]. (4) Synergistic surface state of NPs and support modulation. Apart from obtaining a suitable NP surface state with an excellent intrinsic activity, the support is likewise a key factor in the generation of SMNCs with high catalytic activities [189–197]. Firstly, the support determines the interactions between the NPs and itself. When the NPs are loaded onto the surface of a support, it is highly expected that their surface states are strongly related to the local surface structure of the support, as both the electronic structure and stability of NPs can be markedly influenced by the support. Secondly, the support can appreciably affect NP dispersion, as well as the mass transfer ability during catalytic processes. Generally, supports with three-dimensional architectures benefit the dispersion and stability of NPs, as well as facilitate the transfer of reactants/products during the reaction. Finally, the electrocatalyst support should display good conductivity, in order to ensure rapid supply/uptake of electrons from NPs and the electrode. This review will hopefully provide valuable insights into the rational design and synthesis of practical SMNCs via green and sustainable approaches, thus, promoting them for cost-effective and scalable applications.

4. Application of SMNCs in the electrochemical HER

As typical heterogeneous catalysts, SMNCs possess larger active surface areas compared to bulk materials, ensuring sufficient active sites for catalytic applications. SMNCs generated by sustainable methods possess a clean environment, avoiding pollution by organic agents, which assures accessibility to the active sites. Moreover, recent advances in the construction of controllable metal NP surface states and shapes have enabled optimization of intrinsic activities of active sites. Furthermore, the suitably synergistic and electronic effect occurring between metal NPs and the support can further tune SMNC activity. Taking advantages of these factors, as well as of their excellent durability and recyclability, over the past few decades, SMNCs have been applied to various catalytic reactions, including water splitting, oxygen reduction, nitrogen fixation, C–H bond activation, CO₂ reduction, nitro group reduction, and C–C coupling, among others (Fig. 14). However, in this section, we will summarize and discuss only the application of SMNCs to the

Fig. 14. Summary of SMNC applications.

electrochemical HER and the accomplishments therein.

Hydrogen is a promising energy carrier, and a potential replacement for fossil fuels, due to its high energy density and clean burning nature [198–201]. Hydrogen production from electrochemical water splitting has been identified as one of the most promising approaches, because of its high efficiency and sustainable characteristics [202–205]. However, the process is significantly impeded by the high overpotential required to achieve it. In order to improve the energy conversion efficiency, the development of efficient catalysts for reducing the overpotential is critical. Presently, Pt-based nanomaterials are catalysts of choice for the HER [206–209]. Considering their high cost and limited availability, it is imperative to develop alternatives that are highly electrochemically efficient. Recently, other Pt-group metals (e.g., Rh, Ru, Ir) and non-noble metal-based SMNCs have shown considerable potential as HER catalysts (Table 2), owing to their relatively low-cost and comparable catalytic performance to that of Pt-based catalysts. In this section, selected representative examples of SMNCs for the electrochemical HER are introduced and their achievements discussed.

For the development and design of excellent electrocatalysts, an in-depth understanding of the HER pathway is crucial. Generally, the HER process consists of a two-step procedure, including the formation of an active H via the Volmer step, and the generation of H₂ via the Heyrovsky or Tafel step, or both (Fig. 15) [210–212]. In other words, the mechanism that triggers the HER process is either the Volmer-Heyrovsky, or the Volmer-Tafel pathway. In contrast to acidic media, in basic or neutral media the O–H bond in H₂O should be split prior to H absorption during the Volmer pathway, which is more challenging than the reduction of active H. Consequently, acidic conditions are more favorable for H₂ production by the electrochemical HER compared to alkaline/neutral conditions, due to the abundance of H⁺ on the catalytic surface.

In acidic conditions, FeP/CNT samples (typical SMNCs) synthesized *via* IL-assistance were the first to be employed as electrocatalysts for exploring their HER activity (Table 2) [156]. As the Fe atoms were highly dispersed in IL molecules, the produced metal NPs featured a small size and a good dispersion, which ensures an abundance of accessible active sites. Along with favorable catalyst structures for efficient electron and mass transport, all fabricated samples displayed outstand-

ing HER activities in acidic media. Specifically, FeP_{MBMG}/CNT, prepared with MBMG-Br and trichloroferrate (III) ILs, exhibited the highest HER catalytic activity in 0.5 M H₂SO₄, having the

Table 2

Summary of HER activity of sustainably produced SMNCs.

Catalysts	Electrolyte	Overpotential at 10 mA cm ⁻² (mV)	Tafel slope (mV dec ⁻¹)	Ref.
Ru NP/C	1.0 M KOH	69	33	[67]
Rh NP/C		7	19	
Ir NP/C		109	42	
Ru@GnP	0.5 M H ₂ SO ₄	13	30	[68]
	1.0 M KOH	22	28	
AuPd NCs/g-C ₃ N ₄	0.5 M H ₂ SO ₄	29 (η_{30})	47	[89]
Rh NP/PC	0.5 M H ₂ SO ₄	21	34	[98]
	1.0 M KOH	33	—	
Ru NP/PC	0.5 M H ₂ SO ₄	63	63	
	1.0 M KOH	30	—	
Ir NP/PC	0.5 M H ₂ SO ₄	30	35	
	1.0 M KOH	110	—	
Cu-doped g-C ₃ N ₄	0.5 M H ₂ SO ₄	390	76	[143]
FeP _{MBMG} /CNT	1.0 M KOH	70	75.9	[156]
AuPt alloy/rGO	0.5 M H ₂ SO ₄	19.7	34	[160]
Ru@C ₂ N	0.5 M H ₂ SO ₄	13.5	30	[215]
	1.0 M KOH	17	38	
RuP ₂ @NPC	0.5 M H ₂ SO ₄	38	38	[216]
	1.0 M PBS	57	87	
	1.0 M KOH	52	69	
Co-NRCNT	0.5 M H ₂ SO ₄	14	69	[218]
	1.0 M PBS	33	—	
	1.0 M KOH	16	—	
Ru@Co-SAs/N-C	1.0 M KOH	7	30	[219]
NiO/Ni-CNT	1.0 M KOH	> 100	51	[227]
Ru _{fcc} /g-C ₃ N ₄	0.1 M KOH	79	—	[228]
CuRu/CB	1.0 M PBS	91	46	[230]
	1.0 M KOH	85	43	
Ni-rGO/Ni foam	1.0 M NaOH	36	77	[231]
RuCo@NC	1 M HCl	28	31	[232]
MoS ₂ -N-GQDs-rGO	1.0 M KOH	186	53	[233]
Carbon-shell-coated FeP	0.5 M H ₂ SO ₄	71	52	[234]
NC/Co/CoP/CP	1.0 M KOH	208	81	[235]
CoO _x @CN	1.0 M KOH	232	—	[236]
Fe ₃ C-Mo ₂ C/NC	0.5 M H ₂ SO ₄	116	43	[237]
Fe ₂ P@rGO	0.5 M H ₂ SO ₄	101	55.2	[238]
CoS ₂ @MoS ₂ /RGO	0.5 M H ₂ SO ₄	98	37.4	[239]
NiSe@NC	0.5 M H ₂ SO ₄	123	53.3	[240]
	1.0 M KOH	250	55.3	
	1.0 M PBS	300	66.2	
MoS ₂ /MGF	0.5 M H ₂ SO ₄	90	42	[241]
g-C ₃ N ₄ /Cu ₃ P	1.0 M KOH	67	45	[242]
TC@WO ₃ @g-C ₃ N ₄ @Ni-NiO	0.1 M NaOH	535	246	[243]
Ru-RuO ₂ /MoO ₃ CNRs	1.0 M KOH	9.2	37	[244]
Ru/NC	1.0 M KOH	21	31	[245]
FeNi@N-CNT/NCSS	1.0 M KOH	203	116	[246]
Ru-RuO ₂ /CNT	1.0 M KOH	12	30	[247]
Ni-Fe-P@C NRs	1.0 M KOH	79	92.6	[248]
Mo ₂ C@C	0.5 M H ₂ SO ₄	141	—	[249]
Mo ₂ C@NC	0.5 M H ₂ SO ₄	60	60	[250]
Ni/CeO ₂ /CNTs	1.0 M KOH	91	—	[251]
Co-doped graphene	0.5 M H ₂ SO ₄	180	82	[252]
WO ₂ /carbon nanowires	0.5 M H ₂ SO ₄	58	46	[253]
Fe-Ni ₃ C@C	1.0 M KOH	292	41.3	[254]
CuCo@NC	0.5 M H ₂ SO ₄	145	79	[255]
rGO@CoNiO _x	0.1 M KOH	320	45	[256]

(To be continued)

Table 2 (continued)

Catalysts	Electrolyte	Overpotential at 10 mA cm ⁻² (mV)	Tafel slope (mV dec ⁻¹)	Ref.
Ni ₃ Fe@N-C NT/NFs	1.0 M KOH	72	98	[257]
CoP@NC-NG	0.5 M H ₂ SO ₄	135	59.3	[258]
Fe ₃ C-GNRs	1.0 M KOH	49	46	[259]
CoSe ₂ -CNT	0.5 M H ₂ SO ₄	174	37.8	[260]
Ru@CQDs	1.0 M KOH	10	47	[261]
Pd-CN _x	0.5 M H ₂ SO ₄	87 (η_{50})	35	[262]
Ru-NC	0.1 M KOH	12	14	[263]
CoSe ₂ @defective CNT	0.5 M H ₂ SO ₄	132	82	[264]
MoSe ₂ /rGO	0.5 M H ₂ SO ₄	125	67	[265]
S-RuP ₂ /NPC	1.0 M KOH	19	41	[266]
	1.0 M PBS	37	53	
	0.5 M H ₂ SO ₄	49	50	
MoSe ₂ /rGO	0.5 M H ₂ SO ₄	210	69	[267]
CNT@MoSe ₂	0.5 M H ₂ SO ₄	178	58	[268]
NiRu@N-C	1.0 M KOH	32	64	[269]
Pt/FeCo al-	0.1 M HClO ₄	18	24	[270]
loy/Cu/CNTs				
Au@NC	0.5 M H ₂ SO ₄	51.4	76.8	[271]
Co-C-N	0.5 M H ₂ SO ₄	138	55	[272]
CoNi@NC	0.5 M H ₂ SO ₄	142	105	[273]
Co ₉ S ₉ @MoS ₂ /CNFs	0.5 M H ₂ SO ₄	190	110	[274]
Ru/PC	1.0 M KOH	21	46.6	[275]
Ru/3DNPC	1.0 M KOH	15	31	[276]
Rh ₄ P/PNC-m	1.0 M KOH	24	38.4	[277]
Pt ₅ /HMCS	1.0 M KOH	46.2	48.1	[278]
	0.5 M H ₂ SO ₄	20.7	28.3	
A-Ni-C	0.5 M H ₂ SO ₄	34	41	[279]
rGO@NiPd@NC	0.5 M H ₂ SO ₄	56	33	[280]
Cu-Pt/NPCC	0.5 M H ₂ SO ₄	10	—	[281]
Rh/Ni@NCNTs	1.0 M KOH	14	20.7	[282]
	1.0 M PBS	26	56.2	
	0.5 M H ₂ SO ₄	45	37.2	
CoNG/Ru	1.0 M KOH	15	42.9	[283]
GNC/NiCo ₂ O ₄	1.0 M KOH	—	37.6	[284]
NiO/ β -Mo ₂ C/RGO	0.5 M H ₂ SO ₄	270	65.8	[285]
Rh ⁰ /CeO ₂	0.5 M H ₂ SO ₄	42	34	[286]
Rh ₂ P/NC	0.5 M H ₂ SO ₄	9	26	[287]
<i>in situ</i> -Rh/C	0.5 M H ₂ SO ₄	30	28.4	[288]
Rh ₂ P/C	0.5 M H ₂ SO ₄	5.4 (η_5)	—	[289]
P-WN/rGO	0.5 M H ₂ SO ₄	85	54	[290]
Rh ₃ Pb ₂ S ₂ /C	0.5 M H ₂ SO ₄	87.3	45.6	[291]
Ni@Pt/NNPC	1.0 M KOH	33.8 (η_{20})	43.78	[292]
	0.5 M H ₂ SO ₄	76.32 (η_{20})	46.73	
(CoMo) ₂ /graphene	0.5 M H ₂ SO ₄	100	60.8	[293]
Ru ⁰ /TiO ₂	0.5 M H ₂ SO ₄	41	52	[294]
Ru ⁰ /HfO ₂	0.5 M H ₂ SO ₄	75	71	
Ru ⁰ /ZrO ₂	0.5 M H ₂ SO ₄	65	50	
GO@Ni-Cu@NF	1.0 M KOH	70	57	[295]
Co@NC/CC	1.0 M KOH	290	73	[296]
MoSe ₂ /graphene	0.5 M H ₂ SO ₄	92	42	[297]
Pt-NCS	0.5 M H ₂ SO ₄	22	30	[298]
Au/rGO	0.5 M H ₂ SO ₄	44	86	[299]
MoS _x /NCNT	0.5 M H ₂ SO ₄	110	40	[300]
FeP-graphene sheets	0.5 M H ₂ SO ₄	123	50	[301]
Pt-FeNi@C	0.5 M H ₂ SO ₄	50 (η_{21})	21.6	[302]
NiCo ₂ S ₄ @NCNF	0.5 M H ₂ SO ₄	117	94	[303]
Pt/CNTs-ECR	0.5 M H ₂ SO ₄	34	26	[304]
ALD50Pt/NGN	0.5 M H ₂ SO ₄	—	29	[305]
FeCo@NCNTs	0.5 M H ₂ SO ₄	275	74	[306]
CoP/CN	0.5 M H ₂ SO ₄	122	54	[307]

lowest overpotential of 70 mV at 10 mA cm⁻², as well as the lowest Tafel slope of 75.9 mV dec⁻¹ (Figs. 16(a) and (b)).

Medium	Overall reaction	Step	Reaction pathway
Acidic	$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$	Volmer	$\text{H}_3\text{O}^+ + \text{e}^- \rightarrow \text{H}^\cdot + \text{H}_2\text{O}$
		Heyrovsky	$\text{H}_3\text{O}^+ + \text{e}^- + \text{H}^\cdot \rightarrow \text{H}_2 + \text{H}_2\text{O}$
		Tafel	$\text{H}^\cdot + \text{H}^\cdot \rightarrow \text{H}_2$
Alkaline & neutral	$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$	Volmer	$\text{H}_2\text{O} + \text{e}^- \rightarrow \text{H}^\cdot + \text{OH}^-$
		Heyrovsky	$\text{H}_2\text{O} + \text{e}^- + \text{H}^\cdot \rightarrow \text{H}_2 + \text{OH}^-$
		Tafel	$\text{H}^\cdot + \text{H}^\cdot \rightarrow \text{H}_2$

Fig. 15. Reaction pathways in three different mediums for the HER.

In addition to being precursors for the synthesis of SMNCs, ILs have also been used as stabilizers and capping agents. For example, by utilizing [APMIm]Br as the stabilizing and capping reagent, Feng et al. successfully obtained AuPt alloy nano-dendrites, which were highly distributed on the reduced graphene oxide support (AuPt ANDs/rGO) (Table 2) [160]. The as-prepared sample with a well-defined flower-like nanostructure and a small size exhibited superior catalytic activity in the HER in 0.5 M H_2SO_4 , displaying a low Tafel slope (34 mV dec^{-1}) and a low overpotential (19.7 mV) at 10 mA cm^{-2} (Figs. 17(a)–(d)). The finding that its activity was superior to that of monometallic Pt NCs/rGO was attributed to the synergistic effect between Au and Pt at the active sites of AuPt ANDs/rGO, which led to its excellent intrinsic activity, and the distinct

flower-like morphology, which provides an abundance of readily-accessed active sites.

$\text{g-C}_3\text{N}_4$, a typical two-dimensional material rich in nitrogen, has been employed as a support for the synthesis of SMNCs. For example, using $\text{g-C}_3\text{N}_4$ as the support, Feng et al. [89] successfully synthesized AuPd NCs/ $\text{g-C}_3\text{N}_4$ via a simple additive-free one-pot aqueous protocol (Table 2). In the TEM images (Figs. 18(a) and (b)), it can be clearly seen that numerous AuPd NPs with a size of 3.76 nm and a clean surface were evenly formed on the $\text{g-C}_3\text{N}_4$ surface following simple stirring for 0.5 h. Taking advantage of these features, the product exhibited HER catalytic activity in 0.5 M H_2SO_4 with an onset potential of 29 mV and a low Tafel slope of 47 mV dec^{-1} . The activity of this material was evidently superior to that of the control samples (Fig. 18(c) and (d)).

In addition to noble metal-based SMNCs, $\text{g-C}_3\text{N}_4$ was utilized as the support for the production of non-noble metal based SMNCs (e.g., Cu) [213, 214]. Zou et al. [143] found that Cu NPs could be successfully deposited on $\text{g-C}_3\text{N}_4$ via a straightforward low-temperature strategy (Table 2). The developed catalysts displayed high HER electrocatalytic activities in 0.5 M H_2SO_4 . Among them, 0.31Cu- C_3N_4 exhibited the highest catalytic activity, as determined by its lowest overpotential of 390 mV at a current density of 10 mA cm^{-2} and its lowest Tafel slope of 76

Fig. 16. (a) Polarization curves of buck FeP (black), FeP(MBMG) (red), FeP(PVBMG)/CNTs (blue), FeP(AMIM)/CNTs (pink), and FeP(MBMG)/CNTs (green) in 0.5 M H_2SO_4 ; (b) Corresponding Tafel plots. Reproduced with permission from Ref. [156]. Copyright 2017, Wiley-VCH.

Fig. 17. (a, b) TEM images of AuPt ANDs/rGO; (c) Polarization curves obtained from AuPt ANDs/rGO (curve a), Pt NCs/rGO (curve b), and Pt/C (curve c) in 0.5 M H_2SO_4 ; (d) Corresponding Tafel plots. Reproduced with permission from Ref. [160]. Copyright 2017, Elsevier.

Fig. 18. (a, b) TEM images of AuPd NCs/g-C₃N₄; (c) Polarization curves achieved from the AuPd NCs/g-C₃N₄ (curve a), Pt/C (curve b), Pd/C (curve c), and bulk g-C₃N₄ (curve d) in 0.5 M H₂SO₄; (d) Corresponding Tafel plots. Reproduced with permission from Ref. [89]. Copyright 2016 Elsevier.

mV dec⁻¹ (Figs. 19(a) and (b)), surpassing noble metal-based SMNCs. Apart from Cu, other non-noble metal-based SMNCs were likewise prepared successfully *via* the same protocol, illustrating the universality of g-C₃N₄, as well as that of the synthetic method.

The above-discussed examples illustrate that certain SMNCs exhibit superior performances in acidic electrolytes, while they may not be suitable as HER catalysts in alkaline or neutral media [215]. Therefore, for industrial applications, it is essential to explore HER electrocatalysts capable of excellent performances at a wide pH range.

As a typical SMNC, Ru@GnP, synthesized via the ball milling method, has been evaluated as a HER electrocatalyst in acidic and basic media (Table 2). It was found that Ru@GnP displayed excellent catalytic activity with overpotentials of 13 and 22 mV at 10 mA cm⁻² in 0.5 M H₂SO₄ (Figs. 20(a) and (b)) and 1.0 M

Fig. 19. (a) Polarization curves of pure C₃N₄, 0.12 Cu-C₃N₄, and 0.31 Cu-C₃N₄ in 0.5 M H₂SO₄; (b) Corresponding Tafel plots. Reproduced with permission from Ref. [143]. Copyright 2015, Elsevier.

KOH (Figs. 20(c) and (d)), respectively, which were appreciably lower than that of the benchmark catalyst Pt/C [68]. The high catalytic activities were predominantly attributed to the fast HER kinetics of Ru@GnP, evidenced by the lower Tafel slopes of Ru@GnP compared to that of the commercial Pt/C catalyst. Additionally, the as-synthesized Ru@GnP retained its activity for the most part in both acidic and basic solutions after long-term cycling tests, suggesting its superior stability. Interestingly, it was discovered that the introduction of nitrogen into GnP in this case led to a deterioration in the HER activity, as nitrogen-doping blocked the metal centers, thereby limiting their exposure at the three-phase interface.

Recently, Ru@C₂N was dedicatedly developed *via* a one-pot polycondensation reaction at a low pyrolysis temperature, using hexaketocyclohexane (HKH), hexaaminobenzene (HAB) trihydrochloride, and RuCl₃ as the precursors (Table 2) [215]. In addition to obtaining Ru NPs in a small size and uniform dispersion to achieve high HER activity, the two-dimensional C₂N layer with evenly distributed holes (0.83 nm) could also anchor active centers and enlarge the active areas, thus, further improving HER activity. As expected, as-prepared Ru@C₂N exhibited excellent HER activity in both acidic and basic media (13.5 mV at 10 mA cm⁻² in 0.5 M H₂SO₄; 17.0 mV at 10 mA cm⁻²

Fig. 20. Polarization curves and corresponding Tafel plots for various samples in 0.5 M H₂SO₄ (a, b) and 1.0 M KOH (c, d). Reproduced with permission from Ref. [68]. Copyright 2018, Wiley-VCH.

in 1.0 M KOH). Moreover, the HER activities of Ru@C₂N were superior to those of other metal NPs (e.g., Co, Pt, Ni, Pd) with C₂N in both acidic (Figs. 21(a) and (b)) and basic media (Figs. 21(c) and (d)). To explore the HER activity of Ru@C₂N under basic conditions, the binding energies were carefully calculated by DFT for H₂O, H, and OH, interacting with Pt₅₅, Ru₅₅, and Ru₅₅@C₂N. In the case of metallic Ru₅₅, the binding energies of H₂O (0.58 eV) and H (0.54 eV) were very close to that of metallic Pt₅₅, however the OH binding energy (0.46 eV) surpassed that of Pt₅₅ (−0.49 eV) significantly, resulting in decreased HER activity. However, when the C₂N was present as the matrix, the M-H₂O binding energy of Ru₅₅@C₂N (near face: 1.45 eV; top: 0.69 eV) was markedly higher than that of metallic Ru₅₅ (0.58 eV) and Pt₅₅ (0.59 eV), leading to an acceleration in the rate of H₂O adsorption and dissociation, and thereby an enhancement in the HER performance in alkaline solution (Figs. 21(e) and (f)). Moreover, these HER activities were comparable or superior to those of Pt-based SMNCs in a wide range of pH values.

Another representative SMNC for the electrochemical HER in alkaline medium was reported by our group (Table 2) [67]. As described above, the synthesized M (M = Rh, Ru, Ir) NP/C was small in size, displayed a clean surface, and was extensively deposited on the carbon matrix. As a catalyst for HER, Rh NP/C displayed optimal HER activity in 1 M KOH, based on the lowest Tafel slope and the highest turnover frequency (TOF); however, the Ir NP/C exhibited the lowest HER activity, having the highest Tafel slope and the lowest TOF (Figs. 22(a)–(d)). Moreover,

Fig. 21. Polarization curves and corresponding Tafel plots for various catalysts in 0.5 M H₂SO₄ (a, b) and 1.0 M KOH (c, d). H₂O adsorption of Ru₅₅@C₂N (top) (e) and Ru₅₅@C₂N (near surface) (f). Reproduced with permission from Ref. [215]. Copyright 2017, Macmillan Publishers Limited, part of Springer Nature.

the developed catalysts exhibited a high stability for the HER in basic solution with no structural changes being observed after 1000 CV cycles. Furthermore, inspired by the excellent HER performance of Rh NP/C, we assembled a water-based electrolytic cell (1 M KOH) with Rh NP/C as the cathode to assess its practical applicability. As expected, the as-assembled electrolyzer required a voltage of only 1.53 V to attain 10 mA cm^{−2}, comparable to the cases of majority of reported catalysts utilized in overall water splitting. This electrolyzer additionally displayed outstanding stability, as no noticeable changes in the current density were detected after long-term measurements.

Additionally, SMNCs developed by our group *via* the surfactant- and reductant-free (electroless deposition) approach were explored as HER electrocatalysts (Table 2) [98]. Rh NP/PC exhibited the highest HER activity in acidic medium with the lowest overpotential (21 mV) at 10 mA cm^{−2} (Fig. 23(a)), whereas Ru NP/PC was the most suitable HER catalyst in alkaline medium with the lowest overpotential (30 mV) at 10 mA cm^{−2} (Fig. 23(b)). Using Rh NP/PC as the cathode in an alkaline electrolyzer, an output current density of 10 mA cm^{−2} was attained at a low cell voltage of 1.54 V (Fig. 23(c)). Moreover, this electrolyzer displayed good durability during the long-term measurement. When this electrolyzer was connected to a solar cell for the assembly of a light-driven water-splitting system, it achieved a high solar-to-hydrogen efficiency of 17.3% (Figs. 23(d) and (e)).

The HER activities of SMNCs (e.g., RuP₂@NPC [216], RuP@NPC [217], Co-NRCNTs [218], Ru@Co-SAs/N-C [219], Ni₂P@NPCNFs [220]) at the full pH spectrum have likewise been explored in recent years. For example, RuP₂@NPC was produced by a self-assembly procedure using phytic acid cross-linked RuCl₃ (RuPA) as the precursors, followed by thermal treatment of RuPA and melamine in an inert atmosphere (Table 2) [216]. As expected, as-prepared RuP₂@NPC

Fig. 22. Polarization curves (a), activity comparisons (b), Tafel plots (c), and TOF (d) for surface metal sites of Rh NP/C, Ru NP/C, and Ir NP/C; Commercial Pt/C was also presented in (a,b). Reproduced with permission from Ref. [67]. Copyright 2018, Wiley-VCH.

Fig. 23. Polarization curves of various catalysts in 0.5 M H₂SO₄ (a) and 1 M KOH (b); (c) Polarization curve of OWS utilizing Rh NP/PC and NiFe-LDH as the cathodic and anodic catalyst, respectively; J-V curves (d) and photo (e) of the solar-driven OWS electrolyzer. Reproduced with permission from Ref. [98]. Copyright 2019, Wiley-VCH.

acted as an efficient HER electrocatalyst with a low overpotential (38 mV in 0.5 M H₂SO₄, 57 mV in 1.0 M PBS, and 52 mV in 1.0 M KOH) at a current density of 10 mA cm⁻², and a low Tafel slope (38 mV dec⁻¹ in 0.5 M H₂SO₄, 87 mV dec⁻¹ in 1.0 M PBS, and 69 mV dec⁻¹ in 1.0 M KOH) (Figs. 24(a)–(c)). Theoretical calculations revealed that the hydrogen adsorption value of RuP₂@NPC was 0.233 eV, which is close to zero and weaker than that of RuP₂ NPs (−0.627 eV, Fig. 24(d)), C (1.594 eV) and NPC (0.486 eV). This result indicates that the N, P co-modified carbon shell augmented the surface state of RuP₂ NPs, endowing them with a suitable hydrogen adsorption energy, thus, resulting in excellent intrinsic HER activity [221,222].

Moreover, transition metal-based SMNCs have also been utilized as electrocatalysts for exploring their HER activities in a wide range of pH values. Recently, Zou et al. [218] developed cobalt-embedded nitrogen-abundant carbon nanotubes (Co-NRCNTs) *via* heat treatment of Co²⁺-g-C₃N₄ derived from cost-efficient raw materials (dicyandiamide and CoCl₂) (Table 2). The HER activity of as-prepared Co-NRCNTs was evaluated in a wide range of pH values using the traditional three electrode system. As expected, Co-NRCNTs exhibited outstanding HER activity in acidic, neutral, and basic media (Figs. 25(a)–(d)). After a series of careful analyses and control experiments, it could be reasonably concluded that the superior activity was primarily ascribed to nitrogen doping: (1) N atoms with lone-pair electrons interact more readily with reactants (e.g., protons/water) compared to C atoms [223–225]; (2) As the electronegativity of N is larger than that of C, the N dopants would undoubtedly alter the charge density of adjacent C atoms, thus, enhancing the HER activity [226]. Additionally, the metal NPs encapsulated in CNTs reduced the local work of surface C and N atoms, due to the facile electron transfer from the metal NPs to CNTs, which further promoted HER activity.

Interestingly, it was established that the HER catalytic activity of SMNCs could be further improved by combining the

Fig. 24. Polarization curves in 0.5 M H₂SO₄ (a), 1.0 M PBS (b), and 1.0 M KOH (c) for RuP₂@NPC, RuP₂ NPs, Pt/C, and NPC; (d) Calculated free-energy diagram of HER at equilibrium potential. Reproduced with permission from Ref. [216]. Copyright 2017, Wiley-VCH.

nanotubes with other modification strategies, such as heterojunction, nanostructure, exposed facet, and cocatalyst. For instance, Gong et al developed novel NiO/Ni heterostructures supported on carbon nanotubes (NiO/Ni-CNT) (Table 2) [227]. They were prepared by a simple low-temperature thermal treatment, in which the Ni species gradually evolved into NiO on the oxidized CNTs to produce a core shell-like NiO/Ni architecture (Figs. 26(a)–(c)). Surprisingly, as-prepared NiO/Ni-CNT displayed excellent HER activity in basic media, exhibiting a low overpotential at a high current density and a low Tafel slope (Fig. 26(d)). Its excellent catalytic activity was ascribed to the synergistic effect between Ni and NiO species. Regarding NiO on the NiO/Ni interface, the OH⁻ produced from hydrolysis preferentially attaches to interfacial NiO sites by non-ignorable

Fig. 25. Polarization curves of Co-NRCNTs in 0.5 M H₂SO₄ (a), 1.0 M KOH (c), and phosphate buffer (d); (b) Corresponding Tafel plots in 0.5 M H₂SO₄. Reproduced with permission from Ref. [218]. Copyright 2014, Wiley-VCH.

Fig. 26. STEM images (a, b) and schematic illustration (c) of NiO/Ni-CNT; Polarization curves of NiO/Ni-CNT and commercial Pt/C in 1 M KOH (d), $\text{NaHCO}_3\text{-Na}_2\text{CO}_3$ buffer (pH = 10.0) (e), and (f) potassium borate buffer (pH = 9.5). Reproduced with permission from Ref. [227]. Copyright 2014, Macmillan Publishers Limited.

electrostatic affinity; while nearby Ni species would promote proton adsorption, thus facilitating the Volmer process. Additionally, the NiO/Ni-CNT exhibited high HER activities in $\text{NaHCO}_3\text{-Na}_2\text{CO}_3$ and potassium borate buffers (Figs. 26(e) and (f)). Nevertheless, detailed mechanistic explorations of electrocatalysis by the heterostructural NiO/Ni material are restricted, partly owing to challenges in theoretical modeling by DFT of HER reactions in alkaline solutions, which include various charged species.

Furthermore, Zheng et al. [228] studied the pronounced influence of crystalline structure (face-centered cubic, centered cubic, and hexagonal-closed packed) of Ru-based SMNCs on HER catalytic activity (Table 2). Samples with distinct facets were readily obtained by adjusting the temperature and/or pressure. Generally, Ru, a 4d transition metal, possesses a hexagonal-closed packed structure, as reported in the majority of previous studies. To achieve a specific Ru_{fcc} structure, the $\text{g-C}_3\text{N}_4$ substrate was vital, as the addition of $\text{g-C}_3\text{N}_4$ improved metal-support interactions and inhibited the growth of Ru NPs. Electrochemical tests indicated that Ru_{fcc} -based SMNCs possessed superior HER activity in basic electrolyte, with a low overpotential (79 mV) at 10 mA cm^{-2} and a high TOF (4.2 s^{-1} at 100 mA cm^{-2}), which was greater than that of Ru_{hcp} -based SMNCs, as well as that of commercial Pt/C (Figs. 27(a) and (b)). DFT studies verified the superiority of Ru_{fcc} for the HER. The energy barrier of the Ru_{fcc} surface was calculated ($\Delta G_{\text{B}} = 0.41 \text{ eV}$) and found to be lower than that of commercial Pt/C ($\Delta G_{\text{B}} = 0.94 \text{ eV}$) and Ru_{hcp} ($\Delta G_{\text{B}} = 0.51 \text{ eV}$), suggesting that the Ru_{fcc} catalyst had an enhanced water dissociation ability (Figs. 27(c) and (d)) [229]. This result clearly illustrated that facet modulation is another efficient approach for tuning the catalytic activity of SMNCs.

5. Conclusions and perspectives

In conclusion, numerous SMNCs synthesized via sustainable protocols, thus circumventing conventional methods, are capable of significant performance, owing to their economic and environmental advantages, as well as favorable properties. This review summarizes key progress of SMNCs produced by sustainable synthetic methodologies, including their advantages,

preparation conditions, material characteristics, synthetic mechanism, as well as typical applications in electrocatalysis of the HER. Despite significant progress in the field of SMNCs, several key challenges remain and should be addressed in future studies:

(1) The majority of recently reported studies focus on the development of noble metal-based SMNCs, which limits their sustainability and applicability. Additionally, the control of NP loading and size remains challenging. Therefore, more effort should be devoted to developing efficient methods for the control of metal loading and modulation of NP size. Moreover, the development of suitable synthetic routes toward non-noble metal-based SMNCs and the promotion of their applications are important, especially for electrocatalytic reactions. (2) Although numerous strategies have been developed for the synthesis of various SMNCs, the effective control of the surface state of NPs remains challenging, consequently hindering the modulation of their catalytic activities. Apart from exploring novel strategies and adjusting synthetic procedures, the development of a variety of suitable supports/precursors of distinct configurations may enable efficient adjustment of the surface state of NPs. (3) With respect to catalytic activity, the integrated activity of SMNCs can be enhanced via synergistic NP surface state modulation on its own, or combined with crystalline facet modulation, cocatalyst (or heterojunction) construction, and support modulation. (4) Elucidating the relationship between SMNC structure and catalytic activity remains a considerable challenge. The use of in situ technologies for studying this relationship at microscopic or molecular levels would be advantageous. Combined with DFT calculations, it would enable the identification of the relationship and reveal preferred mechanisms for specific reactions.

This review, to a degree, can serve as a rational research reference for the design and manufacture of novel, low-cost, and recyclable SMNCs on a large-scale, and we anticipate new

Fig. 27. (a) Polarization curves of $\text{Ru/C}_3\text{N}_4/\text{C}$, conventional Ru/C , and commercial Pt/C in 0.1 M KOH; (b) Corresponding Tafel plots. (c) Gibbs free energy diagram of HER (ΔG_{H} : hydrogen adsorption free energy; ΔG_{B} : water dissociation free energy barrier). (d) Relationship between the computed ΔG_{H} or ΔG_{B} values and the measured j_0 values on various metal surfaces. Reproduced with permission from Ref. [228]. Copyright 2016, American Chemical Society.

advances in the preparation and practical applications of SMNCs.

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Graphical Abstract

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Sustainable synthesis of supported metal nanocatalysts for electrochemical hydrogen evolution

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A brief summary and perspective regarding the sustainable synthesis of supported metal nanocatalysts and their representative applications for electrochemical hydrogen evolution is provided.

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负载型金属纳米催化剂的可持续构筑及其电催化析氢应用

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摘要: 在众多非均相催化剂中, 负载型金属纳米催化剂(SMNCs)因具有高效、稳定、可循环使用等特性而广泛应用于多相催化反应领域。近几十年来, 研究者们致力于合理设计和优化载体和颗粒等来提高SMNCs催化性能。其中, 通过传统方法(如沉淀法、溶胶-凝胶法、溶剂热法、高温热解法等)成功开发了种类繁多的SMNCs, 然而这些传统方法通常会涉及大量的有机试剂、复杂的制备步骤以及昂贵的专用设备, 极大地限制了SMNCs的规模化生产。因此, 发展简便、高效的绿色可持续的SMNCs生成方法意义重大。本文总结了绿色、可持续化生产SMNCs的几种方法, 包括固态合成法、低温热解法、无表面活性剂和还原剂合成法及离子液体辅助合成法。与传统合成技术相比, 这些方法在可持续性方面、原子利用率方面、产物选择性方面及规模化生产方面表现出明显的优势。此外, 本文还对SMNCs的经典应用-电催化产氢(HER)技术的研究进展进行了详细评述。尽管SMNCs的可持续化合成及其大规模应用已取得较大进展, 但目前仍存在几个关键问题需不断改进: 如何进一步提高绿色、可持续化生产效率? 如何调控金属纳米颗粒的载量及粒径尺寸? 如何调节金属纳米颗粒的表面状态? 如何探究催化剂结构与活性之间的构效关系? 探究上述问题对实现SMNCs的规模化生产及实际应用有着十分重要的现实意义。此外, SMNCs在设计时应遵循协同构建大量的有效活性位和快速的电子传输通道, 协同调控金属纳米颗粒的表面状态、颗粒大小和晶面以及载体和助催化剂的组成和结构。目前报道的大多数SMNCs仅局限于负载型贵金属(Ru, Rh, Ir, Pt等)类, 对此, 我们未来的研究工作应在降低成本、保护环境、规模化生产的基础上将SMNCs拓宽至非贵金属类。此外, 结合理论计算和原位表征技术从本质上揭示SMNCs的构效关系、应用反应机理以及真正活性中心, 拓展其更广的催化应用领域。

关键词: 负载型金属纳米催化剂; 可持续化制备; 绿色合成; 电催化; 析氢反应

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