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Review

Amorphous nanomaterials in electrocatalytic water splitting

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ABSTRACT

Electrochemical water splitting, as a promising method for hydrogen production, has attracted significant attention. However, the lack of an electrocatalyst with a small energy loss and fast reaction kinetics has hindered the development of this technology. Amorphous nanomaterials with short-range order and long-range disorder features have recently shown superior activity compared to their crystalline counterparts in water electrolysis. The enhanced activity arising from their intrinsic disordered structure results in more active sites and a higher intrinsic activity of such sites. In this regard, this review is aimed at summarizing the progress in amorphous electrocatalysts for water splitting. First, the synthesis strategies for amorphous electrocatalysts are discussed. Characterization tools for amorphous nanomaterials are then summarized. Moreover, the origin of the enhanced activity and stability of amorphous nanomaterials is analyzed. Finally, the current challenges and promising opportunities in this research area are discussed. This review aims to provide a guide for designing and developing amorphous nanomaterials with a fascinating electrocatalytic water splitting performance.

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1. Introduction

To date, the consumption of fossil fuels has brought about serious energy and environmental crises. To solve these issues, significant effort has been devoted to utilizing clean energy sources, such as wind, geothermal, solar, and hydrogen [1–11]. Among them, hydrogen energy has attracted increased attention owing to its abundance and high energy density [12–19]. Electrocatalytic water splitting has been regarded as a prospective method for producing hydrogen energy owing to its safety equipment, environmental friendliness, and raw material abundance [20,21]. For the electrocatalytic splitting of water,

1.23 V is applied as the theoretical cell voltage. However, the thermodynamic barriers forbid the proceeding of water splitting unless a large voltage is used, inducing a serious energy loss. An overpotential is an important parameter for analyzing the electrocatalysts performance; that is, the low overpotential represents a high activity. Thus, the development of an efficient electrocatalyst with a small overpotential is critical. An increasing number of researchers have discovered that electrocatalysts are unstable during the reaction process. The surface of crystalline electrocatalysts is occasionally transformed *in situ* into an amorphous structure, which serves as an active species for electrochemical water splitting [22–25]. Subsequently, a

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series of advanced materials with amorphous structures were designed and exhibited a superior performance in terms of water electrolysis compared to their crystalline counterparts [26–28]. Amorphous materials have attracted increased attention in the area of electrolysis. This review focuses on the latest developments in amorphous electrocatalysts for water splitting. The synthesis strategies for amorphous electrocatalysts are first discussed. Methods for characterizing the disordered structure are then provided, and the enhanced mechanisms of amorphous materials are summarized. Finally, challenges and future perspectives in this field are proposed.

2. Synthesis of amorphous nanomaterials

The synthesis methods for amorphous nanomaterials can be divided into two categories. One is the direct preparation of amorphous nanomaterials with short-range order but long-range disorder structures. The other is an indirect synthesis through the treatment of crystalline nanomaterials. During the treatment process, the long-range order structure is broken, whereas the short-range order structure is maintained.

2.1. Direct synthesis of amorphous nanomaterials

Several methods, including electrodeposition, photochemical metal-organic deposition (PMOD), aerosol-spray assisting approach, inverse micelle sol-gel, and hydrothermal, co-precipitation, and oxidation-reduction approaches, have been developed for the direct synthesis of amorphous nanomaterials. Owing to their simplicity, template-free use, low cost, and large-scale production, electrodeposition and co-precipitation have emerged as an efficient technology for synthesizing amorphous nanomaterials [29,30]. For example, amorphous NiFe hydroxides were successfully prepared through the co-electrodeposition of Ni and Fe precursors on a Ni foam support [31]. PMOD is a scalable cut-price technique that can produce amorphous materials with a precise metal composition. For example, Berlinguette *et al.* [32] adopted the PMOD technique to prepare a series of amorphous nanomaterials with a controllable metal composition (including iron, cobalt, and nickel) and studied their effect on the electrocatalytic activity. However, this method requires expensive equipment, toxic organic metal salts, and an extended operation time. By contrast, aerosol-spray assistant technology can produce amorphous nanomaterials with an accurate composi-

Fig. 1. (a) Scheme of processes associated with an aerosol-spray assisted method for the synthesis of amorphous nanomaterials. Reproduced with permission from [33]. Copyright 2014, Wiley-VCH. (b) Illustration of the two-step hydrothermal synthesis of amorphous FeMoS₄ NRA/CC. Reproduced with permission from [37]. Copyright 2017, Royal Society of Chemistry.

tion and continuous output. The composition of metal elements can be easily adjusted by controlling the proportion of metal ions. As a result, the catalytic activity of the products can be optimized. A continuous production is suitable for industrial applications. As shown in Fig. 1(a), Geng *et al.* [33] reported that amorphous Ni-Fe-O_x compounds obtained through aerosol-spray assistant technology showed the best activity when the Fe/Ni ratio was 6/10 (Fe₆Ni₁₀O_x). The productivity of the catalyst was 0.1 g h⁻¹ from a unit device in the lab. The inverse micelle sol-gel technique can be used to prepare amorphous nanomaterials with a mesoporous structure. For example, amorphous Fe₂O₃ with large amounts of mesopores was synthesized by annealing precursors at 150 °C in static air to remove the adsorbed carboxyl and nitrate species [34]. Furthermore, some techniques, including hydrothermal and oxidation-reduction methods, are regarded as efficient for producing amorphous nanomaterials with microporous, mesoporous, nanorod arrays, ultrathin structures, or other favorable morphologies [35,36]. For example, an amorphous FeMoS₄ nanorod array grown on a carbon cloth (called FeMoS₄ NRA/CC) was

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successfully produced through hydrothermal treatment (Fig. 1(b)) [37]. Therefore, the direct preparation technology is simple, convenient, and easy to operate, and can acquire favorable morphologies and accurately control the concentration of each metal element, finally leading to the optimal catalytic activity.

2.2. Indirect synthesis of amorphous nanomaterials

Indirect synthesis methods for amorphous nanomaterials can be divided into *in situ* conversion and *ex situ* conversion based on the relationship between the treatment process and electrochemical test. When a transformation from a crystalline state into an amorphous state occurs during the electrochemical test, it is called an *in situ* conversion synthesis. An *ex situ* conversion refers to the treatment of materials before the electrochemical test.

2.2.1. In situ conversion synthesis of amorphous nanomaterials

The *in situ* conversion synthesis of amorphous nanomaterials depends on two mechanisms. One is a leaching mechanism, and the other is an electro-oxidation mechanism. Yang and co-workers found that the surfaces of LiCoO_2 and LiCoPO_4 can be transformed *in situ* into amorphous oxides, and the latter exhibits an obvious conversion mechanism owing to the leaching of P during the electrocatalytic process (Figs. 2(a–f)) [38]. Following this study, F and S anions with low binding energies also exhibited similar leaching phenomena [39,40]. Along with the leaching process, a large number of defects will be formed and accumulated on the surface of the crystal material. Finally, amorphous materials are formed. Notably, the leaching effect usually does not extend to the interior of the materials because the *in situ* formed amorphous layer protects the internal structure from the erosion of the electrolytes. In addition to anion

leaching, this mechanism can also be extended to cation leaching. For example, the leaching of Y and Mn ions from the surface of $\text{Y}_2\text{Ir}_2\text{O}_7$ (Fig. 2(g)) and CoMn-LDH also produces amorphous regions [41,42]. Moreover, the electrocatalytic process might induce the oxidation of materials driven by the external potentials. Because an oxidation layer formed *in situ* is thin and the electro-oxidation process ends within an extremely short period of time, its order structure is terminated within a short range, inducing an amorphous structure. For example, the surface of Ni_2P is transformed *in situ* into an amorphous-likely NiO_x with a thickness of only 11 nm during the electrocatalytic process (Figs. 2(h–l)) [43]. Recent studies found that, during the electrocatalytic oxygen evolution reaction (OER) process, the surfaces of the metal phosphates, sulfides, nitrides, oxides, and selenides can also be transformed into amorphous oxides or hydroxide films [22,23,44–47]. Although an actual active phase is obtained during the *in situ* conversion process, the details are unclear owing to the limited characterization technologies available to date.

2.2.2. Ex situ conversion synthesis of amorphous nanomaterials

When the size of the materials is extremely small, the degree of crystallinity becomes weak owing to the high surface energy [48]. Thus, amorphous nanomaterials can be prepared by breaking the crystalline materials of a long-range order into small pieces. For example, Zhang's group found that crystalline $\text{Pd}_3\text{P}_2\text{S}_8$ was transformed into ultrasmall lithium-incorporated Pd phosphosulfide nanodots (indicated as Li-PPS NDs) with a lateral size of ~ 2 nm [49]. First, $\text{Pd}_3\text{P}_2\text{S}_8$ was synthesized using a chemical vapor transport technique. The crushed $\text{Pd}_3\text{P}_2\text{S}_8$ fragment was then assembled as the cathode for the controllable galvanostatic lithiation process under mild conditions. Finally, once the de-lithiation process in water (or ethanol) was

Fig. 2. HRTEM images (left) and FFTs (right) of surface regions in LiCoO_2 (a–c) and LiCoPO_4 (d–f): (a) pristine LiCoO_2 , (b) cycled in 0.1M KP, (c) cycled in 0.1 M KOH, (d) pristine LiCoPO_4 , (e) cycled in 0.1 M KP, and (f) cycled in 0.1M KOH. Reproduced with permission from [38]. Copyright 2012, American Chemical Society. (g) Scheme of *in situ* formed amorphous layer through leaching Y^{3+} in $\text{Y}_2\text{Ir}_2\text{O}_7$. Reproduced with permission from [42]. Copyright 2017, American Chemical Society. (h) HRTEM image of Ni_2P nanoparticles after electrochemical OER measurement for 1 h; inset: FFT of the dotted yellow area. EDX mapping of P (i), O (j), and Ni (k), and combined (l) elemental mapping. Reproduced with permission from [43]. Copyright 2015, Royal Society of Chemistry.

Fig. 3. Scheme of transformation from crystalline $\text{Pd}_3\text{P}_2\text{S}_8$ into amorphous Li-PPS NDs and their electrocatalytic performance. Reproduced with permission from [49]. Copyright 2018, Nature Publishing Group.

completed, the $\text{Pd}_3\text{P}_2\text{S}_8$ crystal was disintegrated and transformed into amorphous Li-PPS NDs (Fig. 3). Thus, all methods used to prepare amorphous nanomaterials have the advantages of cost efficiency, simplicity, a low energy efficiency, and high yield compared with crystals, which is expected to be a feasible technology for preparing ideal electrocatalysts.

3. Characterization of amorphous nanomaterials

Owing to their long-range disordered structure, the characterization of amorphous nanomaterials is still a major challenge. The characterization of amorphous nanomaterials usually involves two steps. The first step is the confirmation of their amorphous structure through a classic X-ray diffraction (XRD) pattern, selected area electron diffraction (SAED), high-resolution transmission electron microscopy (HRTEM), and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM). Among them, XRD, as a typical technique used to evaluate a crystalline material, is mostly applied. In a typical XRD pattern of a crystalline material, the position of the diffraction peak represents the specific crystal plane, and the peak intensity represents the degree of crystallinity. Compared to a crystalline material, an amorphous material shows only a very broad peak or no diffraction peak at all (Figs. 4(a–c)) [50–52]. An HRTEM image shows the lattice fringe of a crystalline material (Fig. 4(d)). In a typical HRTEM image of amorphous nanomaterials, the lattice fringe is absent (Fig. 4(f)). The SAED pattern exhibits a distinct facula or diffraction ring for the crystalline materials, whereas amorphous nanomaterials are endowed with diffusive rings (Figs. 4(e,g)) [26]. The weak signal and inner ring in the SAED pattern suggest a short-range order structure (Figs. 4(h,i)) [49,52]. HAADF-STEM images clearly display an atomic arrangement. For example, the HAADF-STEM image of crystalline Ni-Fe alloy shows a long-range order atomic distribution (> 10 nm),

whereas the amorphous NiFe alloy exhibits only a short-range order structure (< 1 nm) at the atomic level (Figs. 4(j,k)) [52].

After confirming the amorphous structure, the second step was the identification of their species. Energy dispersive spectroscopy (EDX), inductively coupled plasma emission spectrometry, and X-ray photoelectron spectroscopy were first adopted to confirm the elements in the amorphous nanomaterials [53]. On this basis, a series of crystalline nanomaterials can be prepared and used as model materials to analyze the species of amorphous nanomaterials. Raman spectroscopy can be used to analyze the vibrations of various chemical bonds in both crystalline and amorphous nanomaterials. Compared with the well-crystalline sample, the disordered sample exhibited a broader and weaker Raman peak (Fig. 5(a) and (b)) [54–56]. Moreover, X-ray absorption spectroscopy (XAS) is often used to investigate the charge states (valence states) and the local structure (coordination geometry) of different elements in amorphous nanomaterials. For the X-ray absorption near-edge structure (XANES), the absorption peak is usually used to analyze the valence state. For example, the position of the XANES peak shifted from 7717.6 to 7720.6 eV after exposure to 1.35 V for 10 h, suggesting the complete conversion of Co^{2+} ions into Co^{3+} ions. (Fig. 5(c)) [57]. Furthermore, for the Fourier transformation (FT) of an extended X-ray absorption fine structure (EXAFS), the absorption peak shape possesses a fingerprint feature for analyzing the coordination geometry, and the bond length is also provided to recognize the type of chemical bond. As shown in Fig. 5(d), the bonding of Ni in NiSe_2 decorated with amorphous Ni-based oxide (NiSe/NiO) exhibits Ni–O and Ni–Se bonds, confirming that NiSe_2 decorated with amorphous NiO_x can be successfully fabricated [58]. Similarly, Zou *et al.* [59] reported that amorphous $\text{Cu}@\text{CoS}_x$ constituted by the Cu foil and a Co_9S_8 -likely structure was successfully identified using XANES and EXAFS. Notably, both the decreased intensity and oscillation amplitude in XANES and EXAFS may be indexed to a high degree of disorder or an amorphous structure. The intensity of the C peak is reduced in an oxygen-evolving active state (+1.62 V vs. RHE) owing to the formation of an amorphous CoO_x shell during catalysis (Fig. 5(e)) [28]. The SnCoFe-Ar exhibited a less intense oscillation owing to the destroyed crystallinity when using Ar plasma (Fig. 5(f)) [60].

4. Activity origin of amorphous nanomaterials for electrocatalytic water splitting

Amorphous nanomaterials usually exhibit a superior performance compared to their crystalline counterparts in electrocatalytic water splitting. The enhanced activity can be attributed to the more active sites and higher intrinsic activity of a single active site. The isotropic property and re-assembly ability endowed amorphous nanomaterials with high durability.

4.1. Abundant active sites

Increasing the number of active sites was considered a useful and facile method to improve the electrocatalytic activity.

Fig. 4. (a) XRD patterns of amorphous Co/Fe-based (oxy)hydroxide. A-C and A-F indexed to Co-based (oxy)hydroxide and Fe-based (oxy)hydroxide. The Co/Fe ratio of CFeOH-COH-1/3, CFeOH-COH-1, and CFeOH-COH-3 are 1:3, 1:1, and 1:1, respectively. Reproduced with permission from [50]. Copyright 2020, Elsevier. (b) XRD of un-anodized and anodized materials followed by annealing at different temperatures. Reproduced with permission from [51]. Copyright 2016, Royal Society of Chemistry. (c) XRD of amorphous and crystalline Ni-Fe alloy. Reproduced with permission from [52]. Copyright 2020, American Chemical Society. (d) HRTEM image of crystalline CoFe_2O_4 . (e) The corresponding SAED of (d). (f) HRTEM image of amorphous CoFe_2O_4 ($n \sim 3.66$). (g) The corresponding SAED of (f). Reproduced with permission from [26]. Copyright 2014, American Chemical Society. (h) HRTEM image and SAED of amorphous Li-PPS NDs. Reproduced with permission from [49]. Copyright 2018, Nature Publishing Group. (i) HRTEM and SAED of amorphous Fe-Ni alloy. HAADF-STEM images of amorphous Fe-Ni alloy (j) and crystalline Fe-Ni alloy (k). Reproduced with permission from [52]. Copyright 2020, American Chemical Society.

Previous studies mainly focused on adjusting the microstructure of the electrocatalyst to increase the exposure of the active site [61–63]. Researchers have recently found that the design of an amorphous structure can lead to a higher exposure of active sites [64–67]. The amorphous structure easily formed defects

associated with unsaturated atoms. Surrounding these unsaturated atoms (or defect sites) are dangling bonds, which can play a role in active sites [68–70]. In addition, an amorphous structure can extend the active sites from the surface to the bulk of the materials [71]. For example, Klingan *et al.* [72] pre-

Fig. 5. (a) Raman spectra of crystalline and disordered cobalt manganese oxides. Reproduced with permission from [54]. Copyright 2013, Wiley-VCH. (b) Raman spectra of (1) Co_3O_4 -20 h, (2) Co_3O_4 -20 h- H_2O_2 , and (3) Co_3O_4 -20 h- H_2O_2 -Ar, and the crystalline degree decreased from (1) to (3). Reproduced with permission from [56]. Copyright 2014, Wiley-VCH. (c) The XANES spectra of Co K-edge for pakhomovskiyte loaded on FTO electrode, after operation at 1.35 V for 2 min and 10 h. Reproduced with permission from [57]. Copyright 2015, Wiley-VCH. (d) The k^3 -weighted FT spectra of NiSe/NiO, NiSe₂ ultrathin nanowires (NiSe₂ UNWs), NiO, and NiSe. Reproduced with permission from [58]. Copyright 2017, Wiley-VCH. (e) XANES profiles of Co_3O_4 under electrochemical conditions. Reproduced with permission from [28]. Copyright 2015, Nature Publishing Group. (f) Co K-edge FT-EXAFS $k^3\chi$ data of SnCoFe and SnCoFe-Ar. Reproduced with permission from [60]. Copyright 2018, Wiley-VCH.

Fig. 6. (a) OER on the surface of a crystal; (b) OER catalysis in the bulk of amorphous material, and proton transfer to an electrolyte buffer base at the surface; (c) Catalytic currents for variation of the deposition charge from 2 to 200 mC. (d) TOF per cobalt ion and the formed O_2 molecule. Reproduced with permission from [72]. Copyright 2014, Wiley-VCH.

pared a series of amorphous CoO_x films with a thickness range of 15–1500 nm. The electrocatalytic reaction also proceeds in the bulk of amorphous nanomaterials, whereas the crystalline

materials only provide active sites on the surface (Fig. 6(a) and (b)). The protons of the amorphous electrocatalyst are transferred through multiple hopping steps. The current density increases linearly with the deposition charge, and the turnover frequency (TOF) per cobalt ion remains constant (Figs. 6(c,d)), indicating that the activity of the active sites in the bulk is similar to that on the surface. As a result, the number of active sites is proportional to the catalyst volume. Later, Montero *et al.* [57] found that the initially crystalline cobalt phosphate is slowly (over a period of several hours) and finally transformed into amorphous cobalt oxide. They confirmed that both the surface sites and the bulk volume sites of the amorphous catalysts play parallel roles during electrocatalytic water oxidation, whereas the crystalline catalysts only possess active sites on the surface.

4.2. High intrinsic activity

The intrinsic activity of the active sites depends on the activation energy. Optimizing the electronic structure of the materials is an efficient method for improving the intrinsic activity. For example, Zhang and co-workers investigated the electronic structure of Ni-Fe prussian blue analogues before and after electrochemical conversion [73]. As shown in Fig. 7(a), the potential at a current density of 20 mA cm^{-2} continuously decreased over the first 10 h. This process was associated with

Fig. 7. Electrochemical measurement and projected density of states (PDOS) of Ni-Fe Prussian blue analogues. (a) Chronopotentiometric measurement at a current density of 20 mA cm^{-2} ; (b) Polarization curves for different cycles and IrO_2 ; (c) Multi-step deprotonation during OER; PDOS of $Ni(OH)_2$ (d), $NiOOH_{1.5}$ (e), and $NiOOH_{0.5}$ (f). Reproduced with permission from [73]. Copyright 2018, American Chemical Society.

the conversion from crystalline into amorphous nanomaterials. Meanwhile, the linear sweep voltammetry (LSV) curves showed an obvious activity enhancement in the electrocatalytic OER after amorphization (Fig. 7(b)). Fig. 7(c) shows the evolution of the geometric and electronic structures during the deprotonation process. Theoretical simulation results showed that the bandgap in pristine NiFe Prussian blue analogues was ~ 2.5 eV, and the Fermi level was dominated by the Ni-3d states (Fig. 7(d)). Along with the deprotonation (amorphization on the surface), the O 2p component increased to the Fermi level, leading to the evolution of materials into the metallic phase (Fig. 7(e,f)). A similar phenomenon was also found for $\text{SrCo}_{0.85}\text{Fe}_{0.1}\text{P}_{0.05}\text{O}_{3-\delta}$ [74], CoFe-LDH [75], and $\text{Y}_2\text{Ru}_2\text{O}_{7-\delta}$ [76].

The long-range disordered structure at the atomic level provides amorphous nanomaterials with high structural flexibility, leading to an easy dynamic surface self-reconstruction process, which can optimize the surface state for rapid water splitting [71,77]. Meanwhile, the high structural flexibility of amorphous nanomaterials easily allows the catalytically active sites to adopt any required geometry during electrocatalysis, finally improving the activity of a single active site [71]. In addition, the distortion energy on the local structure is critical for the adsorption of reactants and desorption of the products [78,79]. Interestingly, owing to the high structural flexibility and distortion of the local structure, the formation of an adsorption state on the surface of the amorphous electrocatalyst is much easier than that of the corresponding crystalline nanomaterial [66,80,81]. More importantly, a more distorted and flexible local structure can lower the activation energy of the water splitting [82]. For example, Liu and co-workers [77] reported that amorphous cobalt hydroxide nanocages show a high structural distortion, leading to a better catalytic activity than their crystalline counterpart.

4.3. Stability origin of amorphous electrocatalysts

The inactivation of electrocatalysts usually lies in the peeling of substrates at a high current density and/or corrosion during the long-term test. Amorphous nanomaterials generally exhibit a superior stability compared to the corresponding

crystalline catalysts [83–85]. For example, the activity of FeNi phosphides with a thin amorphous layer maintains over 100 h of electrolysis at a high current density of 100 mA cm^{-2} [86]. The amorphous $\text{SrCo}_{0.85}\text{Fe}_{0.1}\text{P}_{0.05}\text{O}_{3-\delta}$ showed a long operational stability of up to 650 h at 10 mA cm^{-2} [74]. The amorphous nanomaterials can easily re-assemble into arbitrary microscopic shapes to intimately contact the substrate. For example, amorphous Ni-Fe alloy showed a superior stability under harsh conditions with a temperature of as high as 80°C and a current density of as high as 500 mA cm^{-2} (Fig. 8(a)) [52]. As shown in the inset of Fig. 8(a), the zigzag line caused by the evolved bubbles of the amorphous Ni-Fe alloy exhibited the least fluctuation, suggesting the high strain and toughness of the amorphous structure (permanently deformed without a fracture at room temperature) [52,87]. Moreover, the isotropic property of amorphous nanomaterials can sustain a high strain of volume change during the redox reaction, particularly in the gas production process, thus improving the corrosion resistance [88]. For crystalline materials, the corrosion quickly started at the grain boundary between the adjacent crystalline grains and then diffused into the inner parts of the materials. The disordered atom arrangement in amorphous nanomaterials guaranteed an isotropic property, which can inhibit the beginning of the corrosion. Xie et al. [89] reported that the thickness of the *in situ* formed active phase (CoO_x) on the surface increased and gradually reached a steady state along with electrochemical oxidation (Figs. 8(b,f)), demonstrating that the formation of an amorphous-like layer on the surface protected the inner crystalline catalyst from further oxidation and/or corrosion.

5. Conclusions and future prospects

This review summarized recent advances in the application of amorphous nanomaterials for electrocatalytic water splitting. First, synthesis strategies and characterization tools for amorphous nanomaterials were briefly summarized. The origin of the superior activity of amorphous nanomaterials was then discussed. Although significant achievements have been made in studies on amorphous electrodes for water splitting, some issues still need to be resolved.

Fig. 8. (a) Chronopotentiometric curves of Ni foam, amorphous, and crystalline Ni-Fe alloy loaded Ni foam at a constant current density (500 mA cm^{-2}) at 80°C . Reproduced with permission from [52]. Copyright 2020, American Chemical Society. HRTEM image of pristine Co_4N (b) without activation, and after 20 (c), 100 (d), 500 (e), and 1000 (f) CV cycles. Reproduced with permission from [89]. Copyright 2015, Wiley-VCH.

(1) An understanding of electrocatalytic water splitting mechanisms over amorphous nanomaterials is critical for the design and production of efficient electrocatalysts. In many cases, the crystalline surface is transformed *in situ* into an amorphous layer during the catalytic process. Thus, an exploration of operando measurements revealing the dynamic formation process and function mechanism for amorphous electrodes will be essential in the future.

(2) Theoretical simulations have been widely conducted to investigate the electrochemical reaction pathway. However, a long-range disordered structure hinders the model building for theoretical simulations. Thus, an advanced characterization tool is urgently needed to establish the short-range order and long-range disorder structures of amorphous nanomaterials.

(3) With an increase in the amorphous state, the number of active sites and their intrinsic activities improve, but the conductivity decreases. An investigation into the effect of the amorphous state on electrochemical water splitting is required to obtain the optimized catalysts. Therefore, a novel technology for adjusting the relationship between the degree of disorder and the conductivity is urgently needed.

Despite some existing challenges in this field, the growing interest in electrocatalytic water splitting using amorphous nanomaterials indicates a promising future. More effort should be devoted to the design of highly efficient nanomaterials and an investigation into their formation and reaction mechanisms. Thus, amorphous nanostructures can be the most promising electrocatalytic materials for water splitting and other electrochemical reactions.

Conflicts of interest

There are no conflicts to declare.

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Graphical Abstract

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Amorphous nanomaterials in electrocatalytic water splitting

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Amorphous nanomaterials have abundant active sites and a high re-assembly ability owing to their short-range order and long-range disorder, which makes them promising electrodes for water splitting.

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非晶纳米材料用于电解水的研究进展

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摘要: 电催化水分解产氢作为一种有前途的制氢技术被全世界研究者广泛关注。然而, 此领域仍然缺少一种高效、无污染的催化剂, 以降低能耗, 提升反应动力学, 进而推进电解水的实际应用。近年来研究发现, 具有短程有序、长程无序特征的非晶纳米材料在电解水领域表现出极其优异的性能。有趣的是, 固有的无序结构赋予了非晶纳米材料丰富的高活性位点。鉴于此, 本文综述了非晶纳米材料的制备策略以及表征方法, 并且对其高活性来源进行了系统地分析。此外, 本文通过分析近几十年的研究成果指出了非晶纳米材料在电解水领域面临的挑战和应用前景。

非晶纳米材料的合成方法主要分为两类: 直接合成和间接合成。直接合成主要包括: 电沉积、光化学金属-有机沉积、气溶胶-喷雾辅助法、反胶束溶胶-凝胶法、水热法、共沉淀法和氧化还原法。其中, 气溶胶-喷雾辅助技术可以通过控制母液中金属离子的浓度精准地控制非晶纳米材料中各种金属元素的组成, 从而有目的地调控并优化催化活性。间接合成主要分为原位转化和非原位转化。原位转化是指晶体材料在反应过程中表面会原位转化为非晶结构作为反应的真正活性物质。非原位转化是指当纳米材料尺度非常小时, 高表面能将会破坏材料的结晶度得到非晶材料。另外, 非晶材料长程无序的特点给其表征带来极大挑战。目前, 对于非晶材料表征的一般流程是: 首先通过X射线粉末衍射确定非晶结构, 并通过透射电子显微镜以及扫描电子显微镜探索其形貌结构; 再通过选区电子衍射以及高角度环形暗场扫描透射电子显微镜进一步确定非晶结构; 然后, 通过能谱、电感耦合等离子体发射光谱和X射线光电子能谱分析其化学组成及化学态; 最后, 采用拉曼光谱和同步辐射数据提供晶体结构信息。

本文对非晶纳米材料高活性的起源进行了探究。在电解水领域, 非晶纳米材料通常表现出优于晶体材料的性能。优异的活性与活性位点数量的增多以及活性位点活性的提升有关: (1)非晶纳米材料具有长程无序的特征, 可以暴露更多活性位点, 并且其表面存在的大量悬挂键也可以作为活性位点; (2)非晶纳米材料的活性位点可以拓展至催化剂体相内部, 大幅提升了活性位点数量; (3)非晶纳米材料结构灵活性高, 活性位点在催化反应过程中可以转变成任意形状, 提升了活性位点的活性; (4)非晶纳米材料的高韧性和应变能力赋予其较高的稳定性。

非晶纳米材料已广泛应用于电解水领域, 但仍然存在一些问题: (1)非晶纳米材料由于原子级结构不确定, 其电催化机理很难探究; (2)理论模拟作为研究电化学反应途径的有力工具很难应用于非晶纳米材料的研究; (3)随着无序程度的增加, 活性位点数量和活性逐渐增加, 但电导率逐渐下降。尽管如此, 由于非晶纳米材料结构灵活性高和自重组能力快速, 人们对其在电解水领域的研究兴趣越来越大, 并且该领域显示出良好的应用前景, 高效非晶纳米材料的设计合成及其催化机理的研究将成为今后研究的重点。

关键词: 非晶; 电催化; 水分解; 合成; 纳米材料

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