

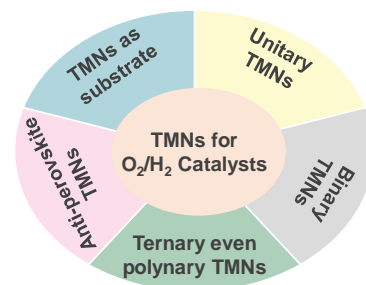
Development of Transition Metal Nitrides as Oxygen and Hydrogen Electrocatalysts

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ABSTRACT With the increasing demand for energy, various emerging energy storage/conversion technologies have gradually penetrated human life, providing numerous conveniences. The practical application efficiency is often affected by the slow kinetics of hydrogen or oxygen electrocatalytic reactions (hydrogen evolution and oxidation reactions, oxygen evolution and reduction reactions) among the emerging devices. Therefore, the researchers devote to finding cost-effective electrocatalysts. Non-noble metal catalysts have low cost and good catalytic activity, but poor stability, agglomeration, dissolution, and other problems will occur after a long cycle, such as transition metal oxides and carbides. Transition metal nitrides (TMNs) stand out among all kinds of non-noble metal catalysts because of the intrinsic platinum-like electrocatalytic activities, relatively high conductivity, and wide range of tunability. In this review, the applications of TMNs in electrocatalytic fields are summarized based on the number of metals contained in TMNs. The practical application potentials of TMNs in fuel cell, water splitting, zinc-air battery and other electrochemical energy storage/conversion devices are also listed. Finally, the design strategies and viewpoints of TMNs-based electrocatalyst are summarized. The potential challenges of TMNs-based electrocatalyst in the development of electrocatalytic energy devices in the future are prospected.

Keywords: transition metal nitrides, hydrogen, oxygen, improvement strategies, electrocatalysts

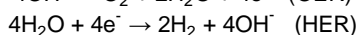
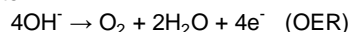


INTRODUCTION

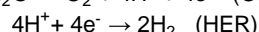
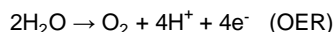
The increasing demand for energy and the aggravation of environmental problems urge scientists not only to find new sources of clean and sustainable energy, but also to develop new energy conversion technologies with high-efficiency, low cost and sustainability.^[1,2] The hydrogen energy is considered as a clean and sustainable alternative to conventional fossil fuels.^[3,4] The water splitting can realize the transformation of electric energy to chemical energy.^[5] Fuel cells, in turn, can convert the chemical energy into electricity.^[6] The reactants and products in the whole reaction process only involve water, hydrogen, and oxygen.^[7] This ensures the cleanliness and environmental requirements of such devices.^[8] Four important basic semi-reactions, namely hydrogen evolution reaction (HER), oxygen evolution reaction (OER),^[9,10] hydrogen oxidation reaction (HOR) and oxygen reduction reaction (ORR), usually occur in electrolytic water devices, fuel cells, zinc-air cells, and so on.^[11] In acidic or basic electrolytes, the reaction process is usually as follows:

HER/OER: $2\text{H}_2\text{O} \rightarrow 2\text{H}_2 + \text{O}_2$

Basic electrolyte:

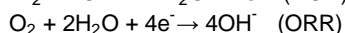
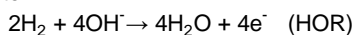


Acid electrolyte:

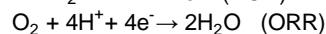
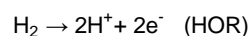


ORR/HOR: $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$

Basic electrolyte:



Acid electrolyte:



Whether in alkaline or acidic electrolytes, the four reactions of H_2/O_2 usually involve multi-step reactions via multiple electrons in the electrocatalysis. Thus, they typically exhibit high kinetic energy barrier due to multi-electron reaction pathways and the large bond energies of H_2O , O_2 and H_2 molecules.^[12] To accelerate the delayed kinetic process of HER, OER, HOR, and ORR, it is necessary to use electrocatalysts, which can improve energy conversion efficiency.^[13,14] So far, precious metals, such as platinum-, iridium- and ruthenium-based catalysts, are still commonly used electrocatalysts.^[15] However, the low crustal abundance of these rare metal electrocatalysts severely limits their commercial applications in energy conversion.^[16] Therefore, there is an urgent need to develop novel electrocatalysts with inexpensive cost and efficient activities for energy conversion.^[17] A common strategy is to introduce supporting materials to maximize the dispersion of precious metals, thereby reducing the use of precious metals while simultaneously increasing the exposed amount when they are utilized as the effective active sites.^[18,19] The resulted precious metal catalysts with low loading can slow down the consumption rate of precious metals.^[20] Another common strategy is to explore non-precious metal materials that are comparable to or exceed the electro-catalytical activities of noble metal-based catalysts as alternatives.^[21] Owing to the abundant reserves and inherent electrocatalytic performance, transition metal-based catalysts have become promising catalysts, such as oxides, phosphates, sulfides or nitrides based on transition metals, etc.^[22] Among them, transition metal nitrides (TMNs) are par-

ticularly outstanding because of the characteristic chemical, physical and electronic properties, etc.^[23] In this mini review, the recent basic fundamental studies of TMNs-based materials used in oxygen and hydrogen electrocatalysts are summarized from unitary TMNs, to binary TMNs, ternary TMNs and even polynary TMNs, as well as the electrocatalysts based on TMNs as supporting materials. In unitary TMNs, researchers mainly improve the material and charge transfer capacity and specific surface area of TMNs by means of morphology regulation to further improve the electrocatalytic activities. The electrocatalytic performances of binary TMNs are enhanced by changing the d-electron state of the parent metal and the number of active sites through heteroatomic doping and heterostructure engineering. As a unique structure, the anti-perovskite TMNs are discussed separately because of the ordered element arrangement, stable crystal structure and similar crystal structure to perovskite oxides. Ternary and even polynary TMNs are also substitutes for efficient electrocatalysts due to the enrich d-electron states and variable d-band centers induced by various transition metal elements. In addition, based on the existing TMNS electrocatalysts, the practical application potentials of TMNS as oxygen and hydrogen electrocatalysts are illustrated by examples. Finally, the challenges and prospects of TMNs-based electrocatalyst are discussed.

TMNs are the interstitial compounds composed of parent metal atoms and nitrogen atoms. The metal atoms are usually arranged in hexagonal close-packed or face centered cubic, while nitrogen atoms with smaller atomic radius are randomly interposed in the gaps of the parent metals.^[24-26] The introduction of nitrogen atoms results in expansion of the original metal lattice and an increase in cell constants. Thus, as the cell constant of the original metal lattice increases, the lattice space between parent metal atoms will also change. Consequently, the interaction between metal and metal atoms weakens, resulting in a corresponding contraction of the *d* orbitals.^[23,24,27] This leads to a redistribution of density of states (DOS) near the Fermi level, an increase in the number of valence electrons, and a change in the structure of the compound.^[28] The redistributed DOS can improve catalytic activities of the parent metal and make it have similar catalytic activities to group VIII noble metals (Ru, Rh and Pd).^[28] Such exceptional crystal structures also enable TMNs to own three bonding characteristics: metallic bond, ionic bond, and covalent bond.^[29] Therefore, TMNs simultaneously possess the properties of metal compounds, ionic compounds, and covalent compounds, such as high conductivity, thermal stability, electrochemical durability and corrosion resistance.^[30] TMNs have been widely used in various energy storage/conversion devices, but there is still almost infinite room for performances in practical applications.

n CLASSIFICATION AND APPLICATION OF TMNS

TMNs-based catalysts are prepared by physical methods, such as plasma,^[31] vapor deposition^[32] and laser methods.^[33] However, the product varieties of TMNs-based catalysts prepared by physical methods usually have some restrictions, such as CrN and

TiN.^[34] However, the morphologies of TMNs prepared by most physical methods are relatively simple. Most of them are thin film structures.^[35] In addition, physical preparation methods are usually complicated and require more demanding conditions, which is not conducive to general synthesis of TMNs.^[35] TMNs-based catalysts can be obtained through chemical methods which usually refer to the nitriding of transition metal oxides,^[36] transition metal layered double hydroxides (LDH),^[37] transition metal inorganic salts^[38] and other metal precursors at high temperature (about 300-2000 °C) and flowing nitrogen (N₂) or ammonia (NH₃) atmosphere.^[28] More specifically, thermal ammonia reduction is usually a gas-solid reaction process which exhibits a mild temperature requirement of about 300-800 °C.^[39] However, the pyrolysis process in N₂ atmosphere requires a higher temperature, about more than 1200 °C.^[39] In addition, TMNs can also be prepared by solvent thermal reactions^[40] or thermal decomposition reactions of polymer precursors,^[41] which usually requires large amounts of nitrogenous compounds, such as small inorganic molecules (such as: urea, melamine, dicyandiamide, etc.)^[42] and organic chemicals.^[43] In short, the preparation of TMNs is a slow solid reaction process.^[25] In addition, the type and number of metal elements, the morphology, the surface structure and the dispersion degree of TMNs will result in different material properties. Therefore, different kinds of TMNs-based materials with different catalytic properties can be prepared by different adjustment strategies, such as changing the type and number of metal elements in TMNs and introducing carriers to form hybrids.

Unitary TMNs. Unitary TMNs are usually compounds formed from only one transition metal element and nitrogen through a specific arrangement and can usually be expressed as A_xN_y. Unitary TMNs usually show conventional structures, such as hexagonal closed packed, face-centered cubic and simple hexagonal.^[27] The researches of unitary TMNs-based electrocatalysts are mainly focused on the regulations of morphology and coordination. Liao's team^[44] reported the limitations of early-transition-metal nitrides (ETMNs) during electrocatalytic ORR from the perspective of O₂, such as ScN, CrN, VN and TiN. The insufficient d electrons and unsatisfactory surface geometries result in that ScN, TiN, CrN and VN have a certain electrocatalytic oxygen reduction ability. In addition, electrocatalytic performances of ETMN nanoparticles are not excellent enough due to the uncontrollable size, morphology, small surface area and easy agglomeration. Therefore, later researchers improved the electrocatalytic performances of TMNs-based electrocatalysts through the regulation of structures with large specific surface area, such as flower- and nanosheet-like morphologies.^[45,46] Cao et al.^[47] prepared vanadium nitride materials with hollow spherical structure (VN HSs) assembled from porous nanosheets by template-assisted method. Compared with bulk VN, VN HSs showed combined structures composited with microporous and mesoporous, larger specific surface area and uniform mesoporous shell structures. The hollow structure facilitated the shortening of the diffusion pathway between molecules and ions close to the catalytic active site, so that it can exhibit high ORR activity. Xie et al.^[46] also fabricated the emerging Ni₃N nanosheets with 2D morphology that are less than 3 nm. Density functional theory

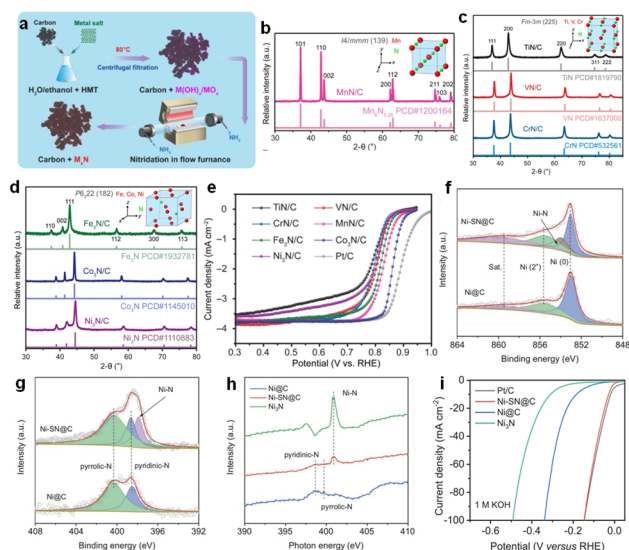


Figure 1. (a) Schematic illustration, (b-d) XRD patterns and (e) ORR LSV tests in O₂-saturated 1 mol·L⁻¹ KOH for carbon-supported TMNs (M_xN/C); Copyright 2022, Science. (f) Ni 2p and (g) N 1s XPS spectra for Ni-SN@C; (h) Synchrotron based N K edge and (i) HER LSV tests in 1 mol·L⁻¹ KOH for Ni-SN@C; Copyright 2021, WILEY-VCH.

(DFT) calculations confirmed that DOS of Ni₃N nanosheets is significantly higher than that of bulk Ni₃N, indicating better carrier concentration and conductivity of Ni₃N nanosheets, also manifesting that the enhanced electrocatalytic performance could be achieved by limiting Ni₃N aggregation. Benefitting from the disorder structure and improved electrical conductivity, Ni₃N nanosheets substantially improved the OER activity compared to bulk Ni₃N catalyst.

Abruna et al.^[48] reported the development of a series of TMNs-based catalysts (Figure 1a). Different electronic structures of transition metals led to distinguishing crystal plane structures, such as MnN, VN, CoN, etc. (Figure 1b-d). Therefore, the TMNs based catalysts with different crystal planes exhibit various electrocatalytic ORR activities. Among them, cobalt nitride-based carbon catalyst (Co₃N/C, Figure 1e) shows the most active catalytic activity with half-wave potential of 0.862 V. When Co₃N/C serves for OER, Co₃N is oxidized to Co₃N@CoO_x with the increase of voltage, eventually forming CoO_x completely. At this point, CoO_x acts as active sites during OER. Qiao et al.^[49] synthesized the new type of nickel-based surface unsaturated nitride (Ni-SN@C, Figure 1f-h) by an unsaturated nitriding strategy. Because of the strong complexation of EDTA and relatively high carbonization temperature, Ni-EDTA directly forms the nickel-carbon core-shell structure at 350 °C to prevent further nitriding of Ni-SN. Unlike ordinary TMNs, the unsaturated Ni-SN@C does not form a long range ordered nitride lattice or metal-metal nitride heterojunction. The Ni-SN@C combines the high activity of metal-based catalysts and the high stability of nitrides at the same time (Figure 1i). In addition, Zhang et al.^[50] reported free-standing nickel nitride/Ni foam (Ni₃N_{1-x}/NF) with abundant nitrogen vacancies via N₂ plasma strategy. N vacancies redistribute the charge in nickel nitride, significantly increasing the

electron density of Ni atoms near the vacancies and lengthening the distance between the valence band maximum and Fermi level. Thus, Ni₃N_{1-x}/NF shows excellent HER activity due to the improved adsorption energy for water molecule, the enhanced adsorption-desorption energy of intermediate (*H) and the accelerated kinetic process brought by abundant N vacancies.

The above work indicates that electrocatalytic abilities of TMNs can be enhanced by changing the morphology to expose more active sites, enhance the transport capacity of electron and material, improve DOS at Fermi level and enhance the carrier concentration and conductivity. Besides, researchers can change the coordination number between metal atoms and nitrogen atoms in TMNs to achieve coordination unsaturation and form metastable phase structure, thus downing the reaction energy barrier of TMNs in electrocatalytic reactions and enhancing the catalytic activities.

Binary TMNs. The electrochemical activities of unitary TMNs are sometimes difficult to exceed that of platinum-based catalysts.^[51,52] Therefore, researchers also typically combine two different transition metals with nitrogen atoms to form binary TMNs. Binary TMNs are mainly focused on TMNs-based heterojunction structure formed by interface coupling and metal atom-doped TMNs. The strategy of metal atomic doping is mainly based on changing the d-electron state of the parent metal nitride through the regulation of electronic structure, then adjusting the gap between the d-band center and Fermi level, and then changing the electrochemical properties of the parent nitride, so as to improve the electrocatalytic activities.^[24,25,52,53] He et al.^[54] designed Co and N co-doped VN (VCoN) nanoplates as ORR/HER electrocatalysts with a one-pot synthetic route. Compared with the pure-phase VN, VCoN nanoplates exhibit a larger specific surface area and possess a higher density of active centers, which guarantee larger contact area between the reactants and VCoN nanoplates, thus achieving enhanced activities. Liao et al.^[44] took VN to propose the strategy of enriching d electrons by doping 3d transition metal to enhance ORR activity. As d orbitals of different transition metal atoms are in different electron-filled states, such as fully filled state, half-filled state, and so on, the ability of acquiring electrons for N atoms is different (Figure 2a). Three electrons transported from the half-filled d orbital of Co atoms to N can lead to significant enrichment of d electrons on the V atom (Figure 2b). This is relatively easier compared to Cu atoms with a fully filled d orbital or Cr atoms with a half-filled d orbital. Compared with other VN based catalysts, the Co doped VN catalyst shows the best performance (Figure 2c-d). Similarly, Liao et al.^[45] also further synthesized hierarchically 3D VCoN micro flowers (VCoN MFs, Figure 2e-g) by the template-free solvent-thermal strategy. The VCoN MFs display high transfer rate of electroactive substances and high utilization rate of active sites. The authors confirmed that ETMNs with d electron deficiency can be promising ORR catalysts by d electron enrichment strategy with d electron-rich doping elements.^[54] Luo et al.^[55] designed the niobium nitride (NbN) nanogrid through nitriding Nb complexes in NH₃ flow. The author proposes that doping the second transition metal (Co) to NbN significantly improves the ORR activity of NbN. The doped Co changes the lattice parameters of NbN and the original

coordination environment, thus changing the ORR performance. Luo et al.^[56] also reported Cr-doped cobalt nitride nanorod array (Cr-Co₄N) as the high-efficiency HER performance. The charge of Cr₄ (+0.717) in Cr-Co₄N is significantly higher than that of Co₄ (+0.211) in Co₄N, indicating that Cr as the doped heteroatoms exhibits a higher positive valence and captures oxygen atoms and further adsorbed H₂O molecules through strong electrostatic attraction. Furthermore, the doped Cr changed electronic structures of pure-phase Co₄N cause d-band center of cobalt atoms to move away from the Fermi level. As a result, the binding interaction between adsorbates and Cr-Co₄N catalysts is weakened, thus enhancing HER activity. In addition, the active sites formed by doping offer more possibilities, which is probably one of the reasons for enhanced activity of the doped cobalt nitride catalyst compared to traditional materials.^[57-59]

To sum up, the doping of the second metals can indeed change the d electron state of the metal atom in parent TMNs. The second transition metal with more d electrons which are not in the fully-filled state or cannot easily become fully-filled or semi-filled state after gaining or losing electrons is more conducive to enrich d electrons for the metal atoms of the parent TMNs. This can effectively change the chemical valence state of metal atoms, shorten, or increase the distance between d-band center and Fermi level, thus improving the electrostatic attraction of TMNs to adsorb species. The doping of the second metals can also change the lattice constant of the parent TMNs and the original coordination environment of metal atoms. All these are effective strategies to improve electrocatalytic activities of TMNs.

Recently, the heterojunction construction can also perfect the selectivity, activity, and stability of TMNs-based materials.^[60,61] The interface coupling phenomenon in the heterojunction structure can lead to lattice distortion and create more active sites through the reconstruction of electronic structure on the parent nitride surface, improving the adsorption capacity of the adsorbent and enhancing the electrocatalytic activities. The heterogeneous interface not only provides more favorable sites for the adsorption/activation of active substances, but also significantly promotes the charge transfer and plays a very high protective role in the exposed active sites.^[62] Heterojunction structures formed by TMNs and different kinds of substances will generate heterogeneous interfaces with different chemical properties, and therefore exhibit different catalytic activities. Fu et al.^[62] developed Ni-V-based nitride heterojunctions anchored by nickel foam as HER catalyst (Ni₃N-VN/NF, Figure 2h-j). DOS of the Ni₃N-VN heterojunction at Fermi level is significantly higher than that of VN and Ni₃N, indicating that the Ni₃N-VN/NF can improve electron mobility and accelerate electron transport. The adsorption capacity (Figure 2k) of the Ni₃N-VN/NF for H₂O is also about twice that of Pt, ensuring the effective adsorption of water on the heterogeneous interface of Ni₃N-VN and providing conditions for subsequent generation of H⁺ and H₂. Ni₃N-VN heterostructure was prepared based on nickel foam, not only achieving the morphology and pore structure regulation of Ni₃N-VN, but also improving the conductivity of Ni₃N-VN/NF catalyst. Rao et al.^[63] also reported interfacial catalytic materials of Ni and Co₂N (Ni/Co₂N) for bi-functional hydrogen (HER/HOR) catalysts. The

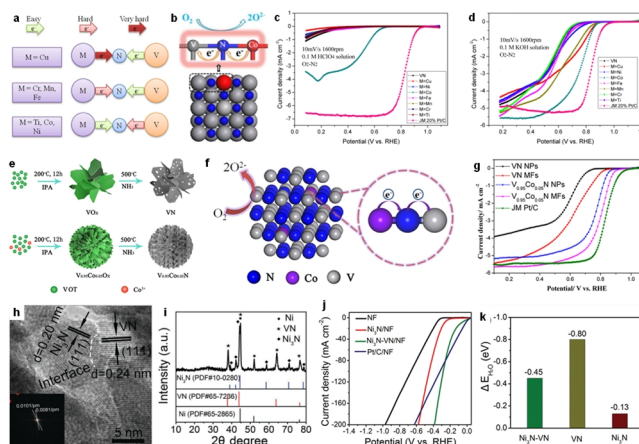


Figure 2. (a) N-determined competitive mechanism; (b) Electron-transfer model of V_{0.95}Co_{0.05}Ns for ORR activity; ORR LSV tests in 0.1 mol·L⁻¹ (c) HClO₄ and (d) KOH for VN and V_{0.95}M_{0.05}Ns catalysts; Copyright 2016, American Chemical Society. (e) Schematic illustration, (f) electron-transfer model for ORR activity and (g) ORR LSV tests in 0.1 mol·L⁻¹ KOH of V_{0.95}Co_{0.05}N MFs; Copyright 2018, American Chemical Society. (h) HR-TEM image, (i) XRD pattern, (j) electrocatalytic HER performance and (k) calculated adsorption energy for H₂O of Ni₃N-VN/NF; Copyright 2019, WILEY-VCH.

formation of Ni and Co₂N interface structure leads to interfacial charge transfer. Thus, the N and Co sites at the Ni/Co₂N catalyst interface is more conducive to adsorbing hydrogen.

Similarly, Lei et al.^[64] also synthesized the N-doped carbon @cobalt-copper nitrides/copper foam nanoarrays (NC@CoN/Cu₃N/CF) with hollow tubular morphology. The NC@CoN/Cu₃N/CF shows fast OER/HER reaction kinetics thanks to highly exposed active sites, abundant “highway” for electron transport, enhanced conductivity, and synergies between cobalt-copper nitrides and copper foam. In addition, Fu et al.^[65] also reported the three-dimensional hierarchical structure with vanadium-nickel-based nitride heterojunctions supported on carbon cloth as the self-standing HER catalyst (VN@Ni₃N-Ni/CC) for water electrolysis. The VN@Ni₃N-Ni/CC hybrids exhibit improved electrolyte diffusion, accelerated gas release rate, and increased reactive plane exposure densities.

Whether for nickel foam, copper foam, carbon cloth, or other types of support materials, they show a number of advantages over powdered catalysts in conventional electrocatalytic reactions. This is because: (1) In electrocatalytic reactions, the conventional powder catalysts are inevitably used in conjunction with the adhesives (such as Nafion) to load onto the electrode surface; (2) Although the actual usage number of adhesives is very small, the usage of binder, to a certain extent, will impede the contact between electrolyte and TMNs-based catalyst, thus reducing the catalytic activities and possibly increasing the over-potential of catalytic reaction;^[66] (3) The different surface properties of various TMNs-based catalysts lead perhaps to the difference of usage effect between catalysts and adhesives. In electrocatalytic reactions, the powdery catalysts also probably fall off from the electrode surface, causing poor catalytic activities.^[67] In addition,

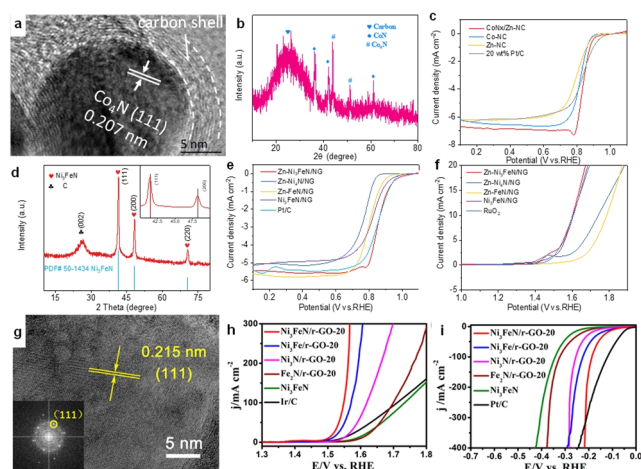


Figure 3. (a) HR-TEM image, (b) XRD pattern and (c) ORR LSV tests in 0.1 mol·L⁻¹ KOH solution of Co₃N/Zn-NC; Copyright 2019, Elsevier. (d) XRD pattern, (e) ORR LSV curves and (f) OER LSV curves in 0.1 mol·L⁻¹ KOH for Zn-Ni₃FeN/NG; Copyright 2021, Royal Society of Chemistry. (g) HR-TEM image, (h) OER and (i) HER LSV curves in 1.0 mol·L⁻¹ KOH for Ni₃FeN/r-GO-20; Copyright 2018, American Chemical Society.

the general price of adhesives is expensive, but also shows a certain toxicity.^[68] Thus, to further improve the application effect of TMNs-based catalysts, researchers have also reported a variety of self-supporting TMNs-based catalysts, such as MXene (the definition: layered 2D metal carbides/carbonitrides),^[68] nickel foam,^[62] copper foam,^[64] carbon fiber/carbon paper^[65] and other supporting substrate materials with good structural/chemical stability and high electrical conductivity. The self-supporting TMNs-based materials can avoid the preparation of working electrode during the testing process, which avoids the use of binder and dispersant, and improves the catalytic efficiency. In addition, in practical applications, such as fuel cells and metal-air cells, the use of collector layer can also be eliminated, thus improving the efficiency of practical applications.

Anti-perovskite TMNs. As a kind of unique nitride, anti-perovskite TMNs possess similar crystal structure with perovskite oxides. Anti-perovskite TMNs exhibit orderly element arrangement, stable crystal structure and high flexibility in composition. The general formula of anti-perovskite TMN is ANM₃, where A is the bivalent or trivalent metal element, and M is the transition metal element.^[43] Anti-perovskite TMNs are usually the Pm-3m type face-centered cubic crystal structure.^[69-72] In theory, each element is orderly arranged. The crystal structure is also stable. Through flexible replacement of A or M elements, electrocatalytic performances of anti-perovskite TMNs-based materials are effectively regulated.^[73] Such materials with rich physical properties like giant magneto-resistance, superconductivity, negative thermal expansion and constant resistivity have already been widely reported, but there are still few studies in the field of electrocatalysis.^[72-74]

As the unique anti-perovskite TMNs, Co₄N exhibits excellent conducting electricity and intrinsic activity for electrocatalytic

reactions. Li et al.^[53] reported Co₄N nanoparticles anchored on porous carbon (CoN_x/Zn-NC, Figure 3a-c) with dual-active-sites through the self-polymerization method of biomass energy and coupling of nitrogen-rich species with metallic ions. Guo et al.^[74] designed and successfully synthesized two-dimensional metallic Co₃FeN nanosheets with porous structures. Due to the synergistic effect of bimetal and the complete exposure of atoms on the side surface and the edge of pore region, the exposed surface has the lowest OH adsorption energy, thus showing enhanced catalytic performance. At the same time, the porous structure can not only accelerate electron transport through the highly oriented crystal structure of metal state, but also facilitate the diffusion of inter-mediate and gases. The enriched two-dimensional hole Co₃FeN nanosheets enhance the catalytic activity. Moreover, Xu et al.^[75] also reported Ni₃FeN-based nitrogen-doped graphene electrocatalyst (Zn-Ni₃FeN/NG, Figure 3d). The introduction of larger Zn atoms changes the lattice parameters of original Ni₃FeN. The resulting stress also changes the electronic structure of Ni₃FeN, thus optimizing the adsorption and desorption capacity of oxygen and corresponding intermediates on the Zn-Ni₃FeN/NG catalyst surface. The Zn-Ni₃FeN/NG thus displays excellent bifunctional ORR/OER activities, where the overvoltage difference is about 0.74 V (Figure 3e-f). Yang et al.^[76] has also prepared the Ni₃FeN catalyst supported on carbon substrate (Ni₃FeN/r-GO-20, Figure 3g) using alginate fibers and rGO via the green and economical method. The bimetallic synergies between metallic Ni and Fe atoms enhance the metallic conductivity of Ni₃FeN. The metal properties and unique core-shell structure of Ni₃FeN also provide more active sites. The coordination between metal and N atoms also promotes electron transfer from the surface of Ni₃FeN cluster to carbon substrate, which not only regulates the surface electronic structure of Ni₃FeN, but also improves the electrocatalytic OER/HER activities of Ni₃FeN/r-GO-20 (Figure 3g-i).

The synergistic effect between metal atoms in anti-perovskite TMNs benefits to improve metallic properties and electrical conductivity. By introducing heteroatoms, the stress effects are generated in anti-perovskite TMNs. And the original electron configuration is changed. Thus, the adsorption and desorption capacity of oxygen-bearing species is promoted on the anti-perovskite TMNs surface. The electron transfer effect can also be produced at the interface of the anti-perovskite TMNs with carbon substrate, thus improving the catalytic performances. However, the surfaces of TMNs are easily oxidized into corresponding hydroxides or oxides, hindering the contact between electrolytes and active sites, decreasing the charge transfer efficiency, and thus resulting in reduced catalytic activities.^[77] Exploring modification strategies for TMNs to enhance their electrical conductivity remains limited, which mostly leads to high overpotential in long running states and unstable catalytic reactions in strong alkaline media.^[77] Therefore, TMNs can be utilized as the catalytic active species to combine with carbon material to form the composite catalyst. Currently, common strategies include introducing carbon support nanomaterials with strong electrical conductivity to form TMNs/carbon composite structures. Carbon support nanomaterials not only protect TMNs from

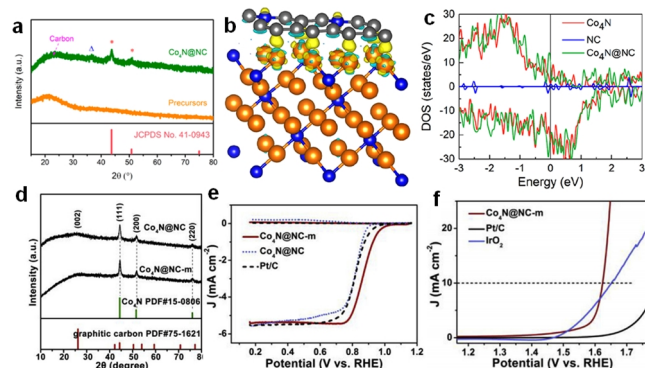
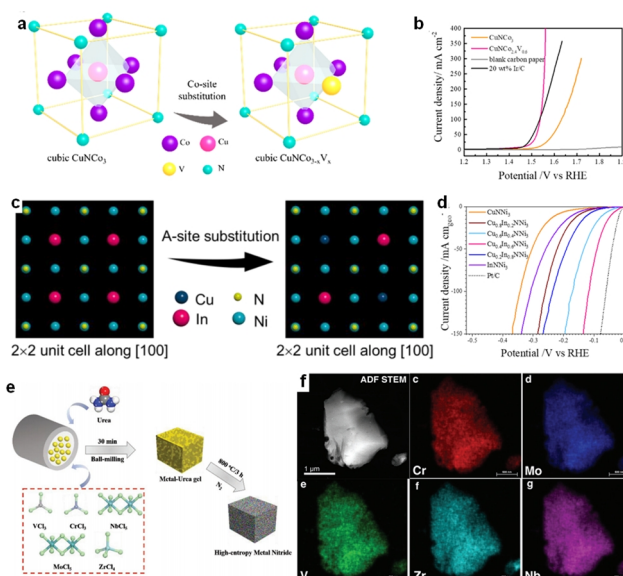


Figure 4. (a) XRD patterns and (b) side view of Co₄N@NC model system (The yellow, gray, and green balls are presented in Co, C and N atoms, respectively.), (c) DOS of Co₄N@NC, Co₄N and NC; Copyright 2020, American Chemical Society. (d) XRD pattern, (e) ORR LSV test and (f) OER LSV test 0.1 mol·L⁻¹ KOH for Co₄N@NC-m; Copyright 2019, Elsevier.

spontaneous aggregation, but also prevent them from accumulating under high temperatures, thereby minimizing the size of TMNs, and maximizing the exposure density of the optimal active sites.^[51] Besides, the doping of heteroatoms into carbon nanomaterials with different electronegativity (c, the c of carbon is 2.55), such as more electronegative nitrogen atoms (c = 3.04), can change the original orbital hybridization state of carbon nanomaterials and the density of electron cloud. The doped nitrogen not only endows carbon nanomaterials more defects, but also regulates the electron distribution state of surrounding carbon atoms.^[78] The combination catalysts of TMNs with carbon nanomaterials can also promote the transfer of charge and oxygen by increasing oxygen pathways, providing more active sites, such as quaternary N with electron donor properties to promote ORR activity, and pyridine N with electron acceptor properties to enhance OER activity.^[79] The synergistic effect between TMNs and carbon nanomaterials is also conducive to improving the electrocatalytic performance of TMNs/carbon composite structures.^[80] At present, numerous researchers have designed highly efficient and stable electrocatalytic O₂/H₂ catalysts by such means. For example, Cheng et al.^[81] designed Co₄N nanoparticles/nitrogen-doped carbon frameworks (Co₄N@NC, Figure 4a-c) hybrids for OER/HER via interfacial engineering strategy. In Figure 6c, Co₄N@NC exhibits higher DOS than Co₄N and NC, indicating significantly increased carrier density during OER/HER charge transfer. The NC, the authors point out, not only facilitates charge transfer, but also provides more active centers. Besides, NC also avoids the surface oxidation of Co₄N, thus preventing a large charge transfer resistance between Co₄N and NC. Synergistic effects between Co₄N and NC also benefit OER/HER. Chen et al.^[82] also took Co₄N as the main active site and then effectively regulated the diameter and dispersion degree of morphology of Co₄N nanocrystalline via melamine, thus improving the utilization rate and inherent activity of Co₄N nanocrystalline. The conductivity and electrochemical surface area of Co₄N are further improved by combining Co₄N nanocrystals with N-doped carbon substrate (Co₄N@NC-m, Figure 4d). The electrocatalytic



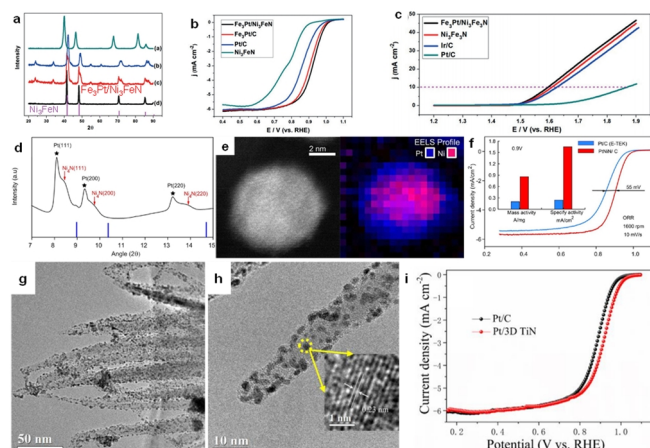


Figure 6. (a) XRD patterns, (b) ORR and (c) OER LSV test in 0.1 mol·L⁻¹ KOH of Fe₃Pt/Ni₃FeN and Ni₃FeN; Copyright 2017, Wiley-VCH. (d) XRD pattern, (e) HAADF image and (f) ORR LSV test in 0.1 mol·L⁻¹ HClO₄ of Pt/Ni₃FeN; Copyright 2012, American Chemical Society. (g-h) TEM images and (i) ORR LSV test in 0.1 mol·L⁻¹ HClO₄ of Pt/3D TiN; Copyright 2019, Wiley-VCH.

Cu_xIn_{1-x}NNi₃ were synthesized by partial substitution of A sites in ANNi₃ (A = Cu or In) by Cu or In. The structures of Pm-3m TMNs are main-tained before and after elemental substitution. However, the lattice constant of ANNi₃ (A = Cu or In) is changed due to the difference of atomic radii between Cu and In before and after elemental substitution. The partially replaced material, Cu_{0.4}In_{0.6}NNi₃, displays better HER activity than unreplaced CuNNi₃ and InNNi₃ catalysts (Figure 5d). The high-entropy metal nitride (HEMN-1, Figure 5e) is also reported by a soft urea template method combined with the mechanical ball milling.^[86] The HEMN-1 exhibits typical cubic crystal structure and contains a variety of metallic components (V, Cr, Nb, Mo, Zr, Figure 5f). This is a new method for the preparation of high-entropy metal nitrides that can extend to other metal components or more metal components. The above doping strategy optimizes the electrocatalytic activities of TMNs. The component regulation provides an effective design idea for the development of other ternary even polynary TMNs-based catalysts. The application can be extended to a wider field of electrocatalysis.

TMNs as Substrate. The different components of TMNs show different catalytic activities, which can be improved by optimizing strategies such as the regulation of metal elements. However, compared with commercial precious metal catalysts, there is still a certain distance. Using TMNs as supporting materials to disperse precious metals can not only significantly improve catalytic activities of TMNs, but also is expected to reduce the consumption rate of precious metals.^[76,87] In addition, the combination of TMNs and noble metal species can also provide multiple active sites, so that designed catalysts can achieve the purpose of multi-functional catalytic activities. Goodenough et al.^[69] designed ordered Fe₃Pt alloys supported by the porous Ni₃FeN substrate (Fe₃Pt/ Ni₃FeN, Figure 6a). For Fe₃Pt/ Ni₃FeN hybrids, Fe₃Pt and Ni₃FeN mainly contribute respectively to ORR activity

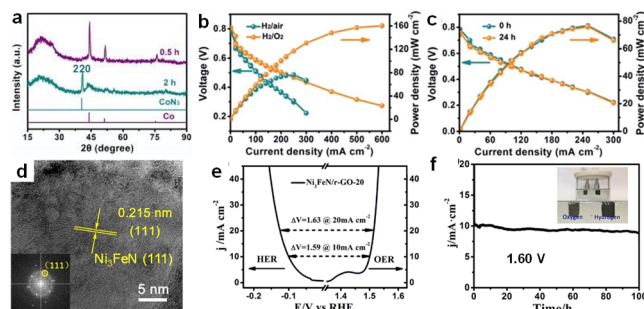


Figure 7. (a) XRD pattern of CoN₃@NC-7-1000, (b) H₂/O₂ and H₂/air fuel cell performances for CoN₃@NC-7-1000, (c) the durability tests of H₂/air fuel cells based on CoN₃@NC-7-1000 catalyst; Copyright 2019, Royal Society of Chemistry. (d) HR-TEM image and (e) HER/OER curves of Ni₃FeN/r-GO-20, (f) the stability test of time-current density for Ni₃FeN/r-GO-20 in a two-electrode configuration at 1.60 V; Copyright 2017, American Chemical Society.

and OER performance (Figure 6b-c). To minimize the usage of Pt, Wang et al.^[88] also designed the PtNiN core-shell structure (PtNiN) for ORR, in which low-content Pt is loaded on the inexpensive NiN core in the form of shell (Figure 6d-e). Nitrogen atom and core-shell structure improve the ORR performance of Pt and provide stability to inhibit dissolution under high oxidation cycle conditions (Figure 6f). The 3D TiN-based nanostructures are also utilized as the support to Pt as ORR catalysts (Pt/3D TiN, Figure 6g-h).^[89] The resulting Pt/3D TiN exhibits superior activities to Pt/C (Figure 6i). The above work manifests that TMNs as the support to load precious metals can not only make precious metals highly dispersed, but also improve the utilization efficiency of precious metals. The high conductivity of TMNs can also be combined with the high intrinsic electrocatalytic performances of precious metals. The resulting TMNs-based catalytic materials generally possess better activities than commercial Pt/C in both acidic and alkaline electrolytes.

Applications of TMNs. Due to excellent electrocatalytic oxygen/hydrogen reaction activities, practical application prospects of TMNs-based materials in energy devices are often explored through assembling metal-air batteries, fuel cells and water splitting devices. Lai et al.^[90] controllably synthesized the CoN₃ nanoparticles/N-doped graphite carbon (CoN₃@NC-7-1000, Figure 7a) by the main exposed crystal surface of (220) via annealing Co/Zn-ZIF-67. Due to stable ORR performance in 0.5 M H₂SO₄ (the half-wave potential of 0.72 V and the high current density retention of 91%), the CoN₃@NC-7-1000 is assembled for hydrogen/oxygen (H₂/O₂) and hydrogen/air (H₂/air) fuel cells to evaluate practical application potential (Figure 7b-c). TMNs are also widely utilized in other metal-air or metal-oxygen batteries. For example, Choi et al.^[91] have synthesized a mesoporous titanium nitride (mesoporous TiN) material with two-dimensional hexagonal structure for Li-O₂ batteries. Excellent electrical conductivity and pore structures make excellent reversibility for the mesoporous TiN-based Li-O₂ battery. Yao et al.^[76] constructed Ni₃FeN embedded reduced graphene oxide (Ni₃FeN/r-GO, Figure 7d) for OER/HER. Benefitting from the high electrical con-

ductivity and fast electronic transport channels of r-GO, the overpotentials of Ni₃FeN/R-GO catalyzed OER and HER are only 270 and 94 mV, respectively (Figure 7e). The overall water splitting is constructed with Ni₃FeN/R-GO catalysts and possessed superior durability (Figure 7f). Zou et al.^[92] prepared amorphous cobalt nitride coupled with nitrogen-doped graphene (CoN_x/NGA) as superior ORR/OER/HER catalysts. The CoN_x/NGA not only drives the zinc-air battery or the water splitting electrolyzer independently, but also integrates the two together to form a self-driven water splitting electrolyzer powered by the zinc-air battery. A hybrid structure of cobalt nitride nanosheets array grown on nickel foam and coupled with N-doped carbon (CoN@NC) was synthesized and reported.^[93] The coupling effect between cobalt nitride and N-doped carbon and the hierarchical porous structure of CoN@NC promoted the mass/electron transport. Thus, the CoN@NC shows enhanced ORR/OER/HER activities. In addition, the CoN@NC displays excellent activity and stability in flexible zinc-air batteries.

n CONCLUSION AND OUTLOOK

As emerging non-noble metal materials, TMNs and corresponding hybrids are outstanding among numerous electrocatalytic materials (such as transition metal alloys-, oxides-, phosphate-based materials, etc.) due to the low resistivity and excellent chemical stability. TMNs not only exhibit combined properties of covalent compounds, ionic compounds, and metal compounds, but also possess electrocatalytic activities like that of group VIII noble metals (Ru, Rh and Pd) due to unique electronic structures of interstitial compounds. In this mini review, TMNs with different metal contents and types are reviewed, such as unitary, binary, ternary and even polynary TMNs and anti-perovskite TMNs. The improvement strategies of electrocatalytic performances commonly used for each type of TMNs are summarized with examples. The catalysts with TMNs as the support dispersed noble metal, other TMNs-based hybrids as electrocatalytic materials, and practical applications in electrocatalytic H₂/O₂ reactions are also reviewed. And the practical applications in H₂/O₂ fuel cells, water splitting electrolyzer and zinc-air batteries are also discussed. Through the above discussion, an efficient and stable electrocatalyst must possess the advantages of suitable electronic structure, low resistivity, exposed active sites as many as possible, and abundant gas/electron transport pathways. However, in this review, the design and construction of TMNs-based materials and the practical application still have some expansion room. Here, we put forward the following discussions on the possible shortcomings of TMNs-based materials:

Synthesis. At present, most synthesis strategies of TMNs-based materials are still achieved through the nitridation of transition metal precursors at high temperature under the condition of N₂ or NH₃. They often increase the preparation cost and make the synthesis pathways more complex and tedious. Therefore, it is necessary to find a simpler, more economical and environmentally friendly synthesis technology. In addition to the modification strategies reviewed in this review, researchers can also devote to controlling the catalytic selectivity by precisely controlling the

exposed crystal surface of TMNs to achieve more efficient catalytic performances. In oxidation reactions, TMNs are usually converted into oxides or hydroxyl oxides at high voltage. Thereby, TMNs can also be utilized as pre-catalysts for in-situ transformation into nitride-core or oxide-shell structure under high potential according to reaction conditions. This is probably more conducive to specific environments of electrocatalytic OER. Meanwhile, advantages of TMNs are also combined with those of oxides. Thus, multi-functional electrocatalytic process is easily realized.

Stability. The catalytic reactions include electrocatalytic hydrogen reaction (HER/HOR) and oxygen reaction (OER/ORR) in this review, and they usually need to be carried out in acidic or alkaline aqueous solutions. However, the stability of metal nitrides in aqueous solutions is usually not ideal, which perhaps polarizes the surface of TMNs-based materials under certain pH conditions. Thereafter, the corrosion resistance of TMNs-based materials to the electrolyte should also be paid attention for enhancing the catalytic stability of TMNs-based materials. This requires researchers to explore more types of substrates with excellent electrical conductivity and abundant electron transport channels for depositing or loading TMNs species, improving the stability. Moreover, TMNs are easily oxidized at high potential. Thus, to maintain the chemical structure and stability, researchers can also build a passivation layer on the surface of TMNs to protect it from being oxidized at high voltage during OER process.

Mechanism. The thorough understanding of catalytic mechanism during electrocatalytic reactions is crucial to constructing efficient and stable TMNs-based materials. The adsorption and desorption processes between TMNs-based materials and reactants, reaction intermediates and electrolytes are usually complex when catalytic reactions take place. In addition, the electrochemical reaction process of TMNs-based materials still lacks detailed research reports. Therefore, researchers can consider strengthening in-situ characterization techniques on TMNs-based materials during HER/HOR and OER/ORR, such as in-situ Raman technology, in-situ infrared spectroscopy and in-situ transmission electron microscopy so as to further understand whether the phase or chemical composition of TMNs-based materials changes during catalytic reactions to facilitate the construction of TMNs-based electrocatalysts.

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n COMPETING INTERESTS

The authors declare no competing interests.

n ADDITIONAL INFORMATION

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