

REVIEW ARTICLE

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Recent progress in palladium-nonmetal nanostructure development for fuel cell applications

Mengjun Wang¹, Leigang Li¹, Mingmin Wang¹ and Xiaoqing Huang¹ 

Abstract

Developing highly efficient and durable electrocatalysts plays a central role in realizing a broad range of fuel cell application. Palladium (Pd)-nonmetal nanostructures, as a special class of Pd-based alloys, have exhibited diversified advantages for fuel cell reactions. In this minireview, the most recent progress in the synthesis of Pd-nonmetal nanostructures and their applications in fuel cells are reviewed. First, the merits and advantages of Pd-nonmetal nanostructures are clarified. Next, strategies for enhancing the performance of Pd-nonmetal nanostructures are summarized by demonstrating the most typical examples. It is expected that this review will generate more research interest in the development of more advanced Pd-nonmetal nanocatalysts.

Introduction

Fuel cells, as a kind of attractive renewable energy conversion device, hold great promise for alleviating the ever-increasing concerns about the energy crisis and environmental issues^{1–5}. Highly active, cost-effective, and durable electrocatalysts are indispensable for driving fuel cell-related reactions, such as the oxygen reduction reaction (ORR) and alcohol oxidation reactions (AORs) (e.g., the methanol/ethanol/formic acid oxidation reactions (MOR/EOR/FAOR))^{6–12}. Platinum (Pt) and its related materials are regarded as state-of-the-art catalysts for enhancing the reaction kinetics of fuel cell reactions, but the scarcity of Pt has restricted its extensive application in fuel cells^{13–16}. As the most promising candidate for replacing Pt, palladium (Pd) has gained ever-increasing attention and research interest for its application in fuel cells^{9,17–20}. However, the intrinsic electronic structure of Pd is not beneficial for achieving an excellent catalytic performance. For example,

the binding strength of Pd–O is too strong to achieve a superior catalytic activity for the ORR^{21,22}.

To address the abovementioned issues, diversified strategies have been adopted to modulate the electronic structures of Pd for catalytic property enhancement, including alloying, strain engineering, defect engineering, and facet control^{23–26}. Recently, the alloying of Pd with nonmetals, such as H, P, S, B, Se, and Te, has received intensive attention for fuel cell applications because of the fascinating merits of Pd-nonmetal nanocatalysts^{27–34}. To date, a wide range of Pd-nonmetal nanostructures has been designed for fuel cell-related reactions (e.g., ORR, MOR/EOR, and FAOR) by adopting different strategies (Fig. 1)^{32,35,36}. This minireview aims to summarize the most recent progress in Pd-nonmetal nanostructure development for fuel cell applications, where the merits of Pd-nonmetal nanocatalysts are first clarified, and then strategies for achieving enhanced catalytic properties of Pd-nonmetal nanostructures are demonstrated.

Why Pd and nonmetals?

The merits of alloying Pd with nonmetals have made it an attractive research topic. First, Pd-nonmetal alloys possess rich phases (e.g., Pd₈Se, Pd₇Se, Pd₄Se, Pd₃Se,

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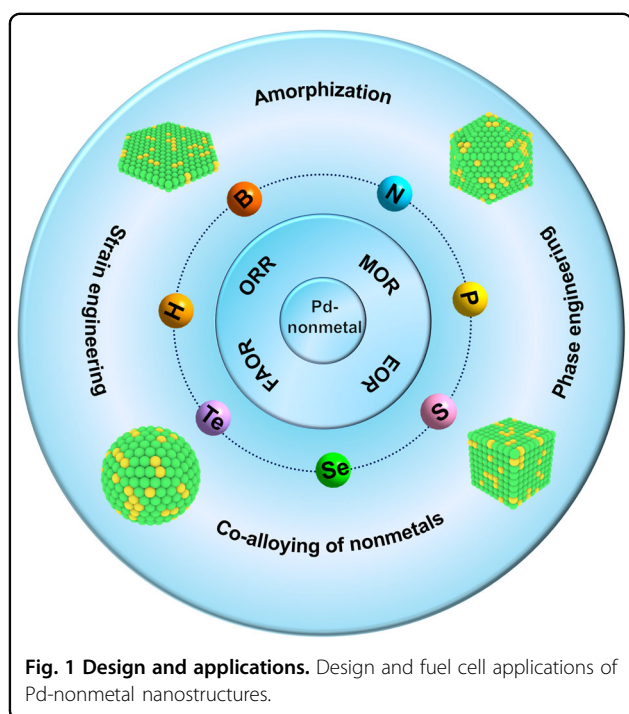
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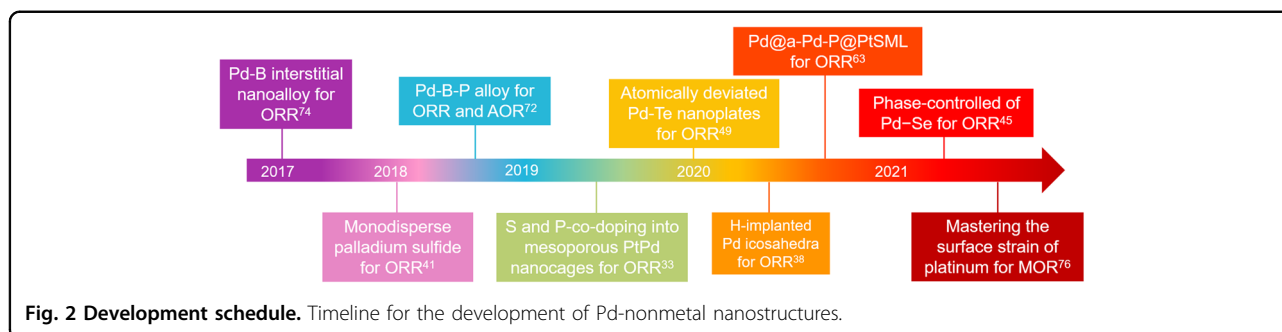
Pd_7Se_4 , PdSe_2 , and $\text{Pd}_{17}\text{Se}_{15}$ for Pd–Se³⁷) compared to Pd-metal alloys, and it is, therefore, possible to tune the catalytic properties by controlling the phases. Second, amorphous phases, featuring abundant surface dangling bonds and defects, can be obtained for Pd-nonmetals under certain synthesis conditions. Third, the nonmetal atoms, for example, H, can be inserted into the crystal lattice of Pd, which can significantly modify its electronic structures and thereby give rise to enhanced catalytic performance³⁸. Finally, the abundant resources, easy access, and low cost of nonmetals are beneficial for the cost reduction of Pd-based electrocatalysts. With the abovementioned merits and advantages, significant progress has been made in the design and synthesis of advanced Pd-nonmetal nanocatalysts for fuel cell applications (Fig. 2). In the following sections, the strategies adopted for the development of advanced Pd-nonmetal catalysts are introduced in detail.

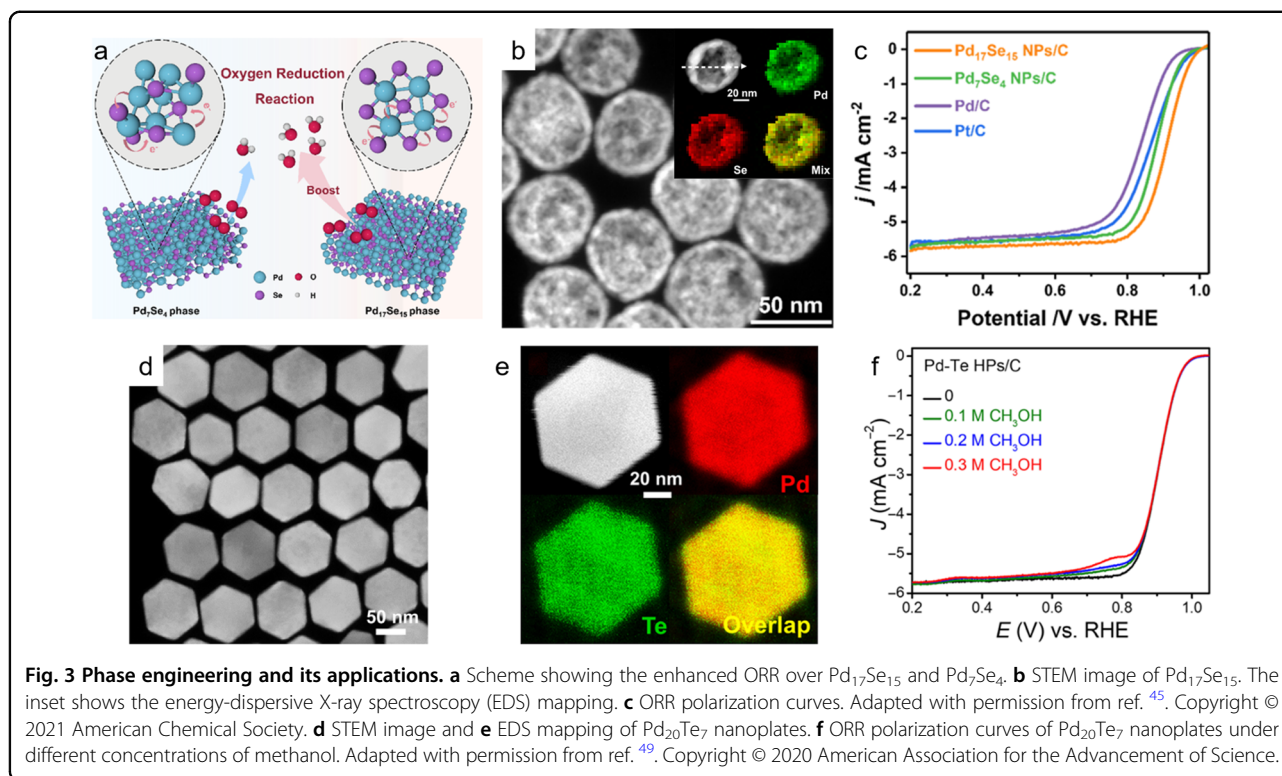


Phase engineering

Different phases/compositions lead to different electronic structures and physicochemical properties, as represented by the Pd–Se and Pd–S systems^{39–44}. The phase engineering of Pd-nonmetals has provided a platform for catalytic performance tuning. A typical example is the crystal phase-dependent ORR performance of the Pd–Se system reported by our group⁴⁵. The $\text{Pd}_{17}\text{Se}_{15}$ phase exhibited a much higher activity and more durable stability for the ORR than the Pd_7Se_4 phase, which could be ascribed to the stronger adsorption of oxygenated species and a greater amount of charge transfer from the $\text{Pd}_{17}\text{Se}_{15}$ surface to the *OOH intermediate (Fig. 3a–c). Sampath et al. prepared different phases of Pd–Se (Pd_4Se , Pd_7Se_4 , and $\text{Pd}_{17}\text{Se}_{15}$) and compared their ORR properties, where Pd_4Se showed the highest ORR activity with fast reaction kinetics⁴⁰. A study on the Pd–S system showed that Pd_4S exhibited the highest catalytic activity toward the ORR among Pd_{16}S_7 , Pd_4S , and PdS , which could be ascribed to the optimal oxygen-binding ability of Pd_4S ⁴¹.

Similar to Pd–Se, the Pd–Te system also possesses rich phases, such as $\text{Pd}_{17}\text{Te}_4$, Pd_3Te , $\text{Pd}_{20}\text{Te}_7$, Pd_8Te_3 , Pd_7Te_3 , Pd_9Te_4 , Pd_3Te_2 , PdTe and PdTe_2 ^{46–48}. Different Pd–Te phases with different Pd/Te ratios possess varied catalytic properties. Controlling the crystal phase to adjust the specific atom arrangement can realize extraordinarily different physicochemical and catalytic properties. For instance, our group synthesized hexagonal $\text{Pd}_{20}\text{Te}_7$ nanoplates (Pd–Te HPs) as a catalyst for the ORR (Fig. 3d–f)⁴⁹. Benefiting from the specific arrangement of the Pd atoms, the $\text{Pd}_{20}\text{Te}_7$ nanoplates displayed superior ORR performance with a high methanol tolerance. Theoretical calculations show that the linear relationship between OOH^* and OH^* was overcome, leaving room for activity enhancement and methanol oxidation suppression. Methanol tolerance is very important for the application of direct methanol fuel cells, and Pd-nonmetals usually possess high methanol tolerance, as also indicated in the Pd–Se system (PdSe , Pd_3Se , and PdSe_2)⁵⁰ and other materials (e.g., Pd_3P , Pd_xSe_y , Pd_xS_y , PdP10)^{11,29,51–53}.





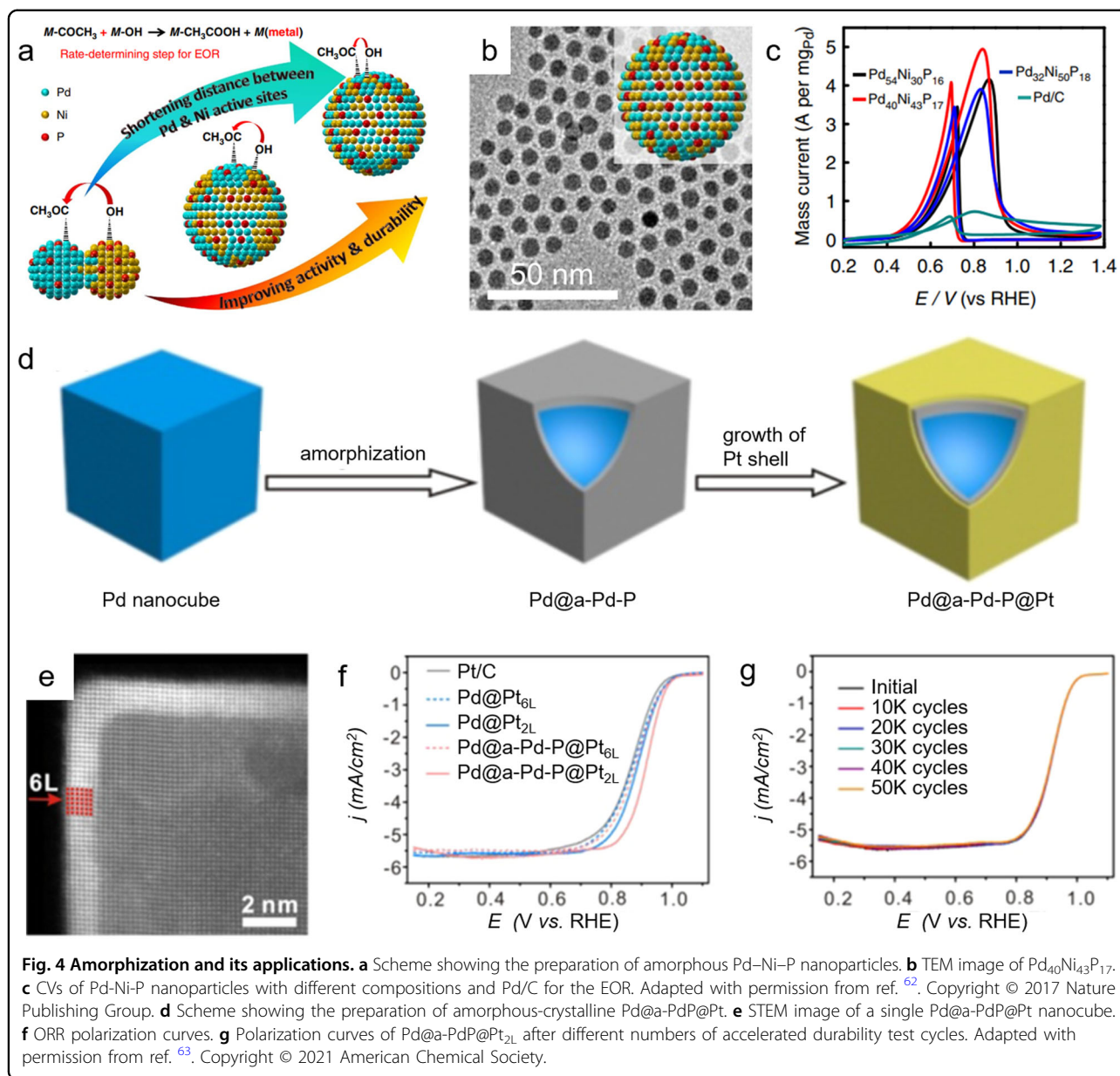
Amorphization

Amorphous materials with short-range ordering are an attractive class of materials with abundant randomly oriented bonds, surface unsaturated atoms, and rich defects, which may benefit catalytic property enhancement^{54–57}. Furthermore, amorphous materials are proven to be highly corrosion-resistant owing to their isotropic properties^{58–61}, which hold great potential for serving as highly active and durable catalysts. Regarding amorphous Pd-nonmetal nanocatalysts, Wang and coworkers prepared ultrasmall amorphous Pd–Ni–P nanoparticles (~5 nm) for electro-oxidation (Fig. 4a–c)⁶². Prolonged phosphorization time induced the formation of amorphous Pd–Ni–P nanoparticles. Although it was stated that the shortened distance between Pd and Ni active sites and optimized Pd/Ni ratio contributed greatly to the superior EOR performance of Pd₄₀Ni₄₃P₁₇, the amorphous nature of the nanoparticles with a disordered structure is believed to play a critical role in enabling the high activity and durable stability. Amorphous materials have been proven to be highly corrosion-resistant, which would be one of the reasons for the enhanced stability. Very recently, an amorphous/crystalline core/shell nanostructure was prepared by Jin et al. for an enhanced ORR with a high activity and ultrastable durability (Fig. 4d–g)⁶³. Pt shells were deposited onto the amorphous Pd@a-Pd-P core, where the number of Pt layers can be tuned. By comparison, Pd@a-Pd-P@Pt_{2L} exhibited the highest activity and most durable stability. It was found

that the amorphous a-Pd-P core is indispensable for realizing the durability of Pd@a-Pd-P@Pt_{2L}. In addition to the abovementioned examples, there are also other reports that demonstrated the effectiveness of amorphous materials in enabling high activity and durability. For example, Asao and coworkers prepared Pd–Ni–P metallic glass (amorphous) nanoparticles for methanol electro-oxidation. The amorphous Pd–Ni–P nanoparticles showed a high stability with only 3.5% activity loss after 400 cycles¹². In addition, Sato et al. synthesized amorphous Pd–P nanoparticles, which also displayed high specific and mass activities toward the ORR compared to crystalline Pd nanoparticles³⁶. All the examples above have clearly demonstrated the power of designing amorphous Pd-nonmetal nanostructures for realizing highly active and durable electrocatalysts.

Strain engineering

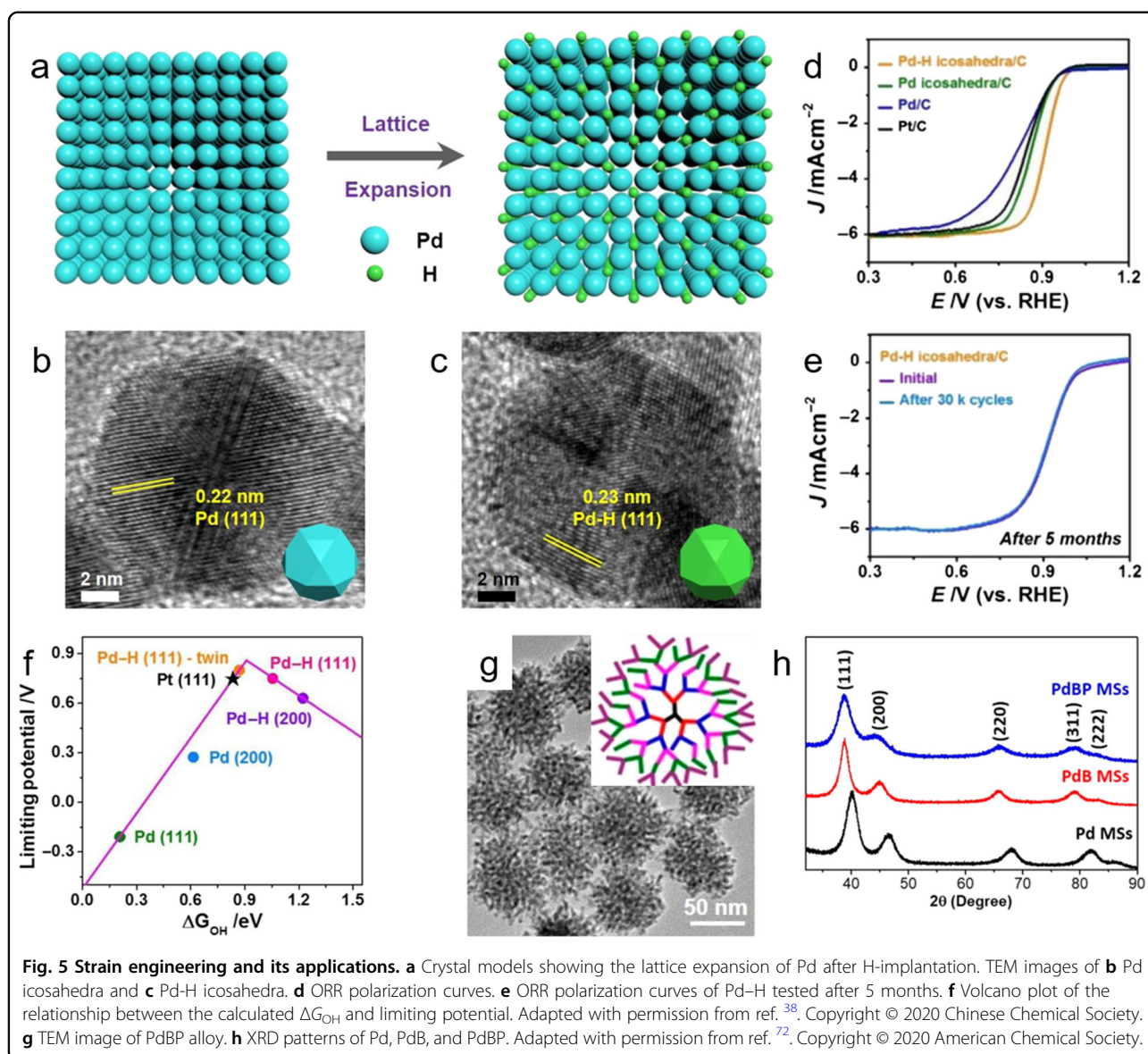
Strain, caused by lattice expansion or contraction, can be used to modify electronic structures, such as the d-band center position, which influences the adsorption of intermediates and catalytic properties^{64–68}. The nonmetals, especially those with small atomic radii, can be “inserted” into the lattice of Pd to tune catalytic performance. Studies of strain engineering for Pd-nonmetals have covered Pd–H, Pd–B, Pd–P, Pb–BP, etc. The H atom, as the smallest nonmetal atom, can be easily implanted into the lattice of Pd to modify physicochemical properties. For example, our group reported H-implanted Pd icosahedra for enhanced



oxygen reduction (Fig. 5a–f)³⁸. The inserted H atoms expanded the lattice and decreased the electron density of Pd, which weakened the Pd–O binding strength. The Pd–H icosahedra showed a much higher activity and more durable stability for the ORR than the bare Pd icosahedra. It was also found that the coordination number of Pd was reduced, and the twinned facet of the Pd–H icosahedra provided an optimal OH binding strength, which worked synergistically to give rise to the superior ORR performance of the Pd–H icosahedra. In addition to H, much work has been done regarding the use of other nonmetals for strain-enhanced catalytic performance, mostly focused on Pd–P, Pd–B, and Pd–P–B^{69–74}. For instance, Chen et al.⁷⁴ and Sato et al.⁷⁵ both reported that B doping expanded the Pd lattice and

weakened O binding, leading to an enhanced ORR performance. In addition, Liu et al. developed a procedure for the synthesis of ternary PdBP mesoporous nanospheres with a highly expanded lattice of Pd for significantly enhanced ORR and MOR (Fig. 5g, h)⁷². The synthesis procedure was also extended to the synthesis of PdMBP (M=Cu, Ag, Pt) mesoporous nanospheres.

More interesting work was performed by Jin et al., where thin Pt shells with tunable lattice strain were deposited on Pd–P cores with different phosphorization degrees (Fig. 6)⁷⁶. In detail, increased tensile strain was created in the deposited Pt shells by increasing the phosphorization degree of the Pd core. At the same time, compressive strain was also generated in the Pt shells by controlling the dephosphorization

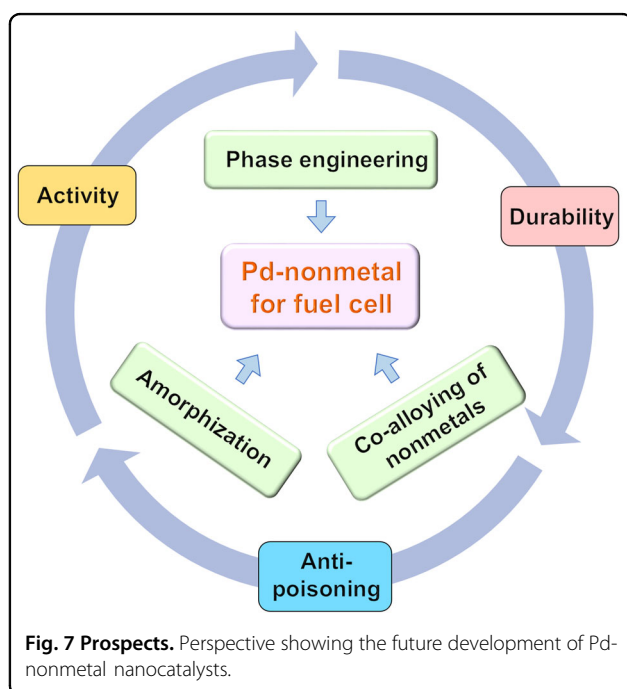
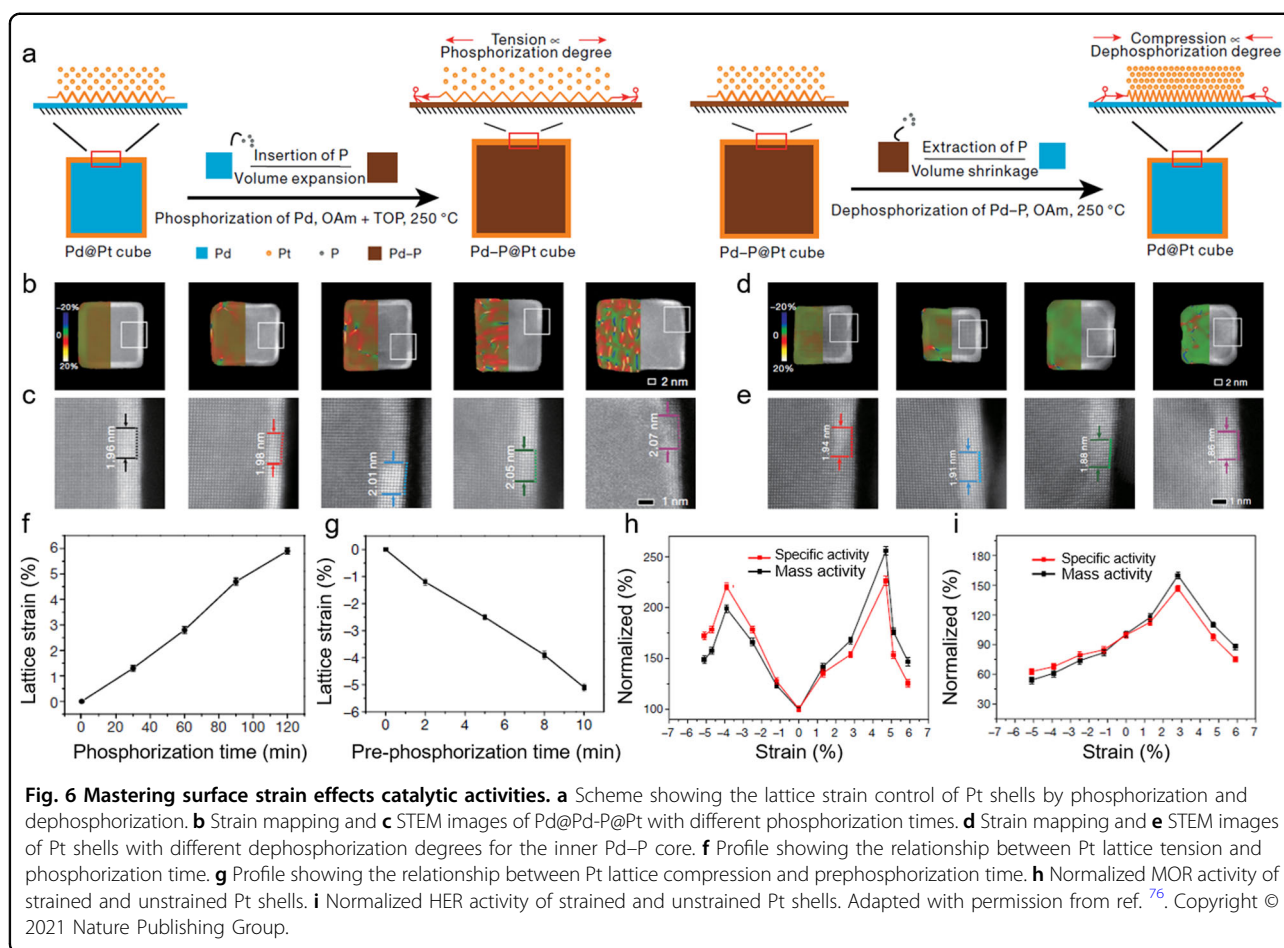


degree of the Pd-P core. The tensile and compressive strains in the Pt shells both highly enhanced the HER activity with a volcano relationship for both cases. For MOR, however, the tensile strain improved the catalytic activity, while the compressive strain decreased the activity, showing a volcano relationship across the compressive and tensile strain range. This work has well demonstrated the power of strain engineering in Pd-nonmetal systems.

Summary and outlook

To conclude, the latest progress in the design and synthesis of Pd-nonmetal nanocatalysts for fuel cell applications is summarized in this minireview. The Pd-nonmetal nanostructures hold great advantages over pure Pd, such as optimized oxygen binding strength, methanol tolerance,

enhanced durability, and reduced cost. It can be summarized that Pd-nonmetal (such as S, Se, Te, H, B, and P) nanostructures are promising candidates for the ORR. The Pd-P and Pd-B structures can also be used as effective EOR/MOR catalysts. Nevertheless, the study of Pd-nonmetal nanocatalysts is far from sufficient. There are still some disadvantages in their synthesis and applications. For example, it is a challenge to find a suitable method for achieving the transformation of the crystal phase or for implanting atoms within the Pd lattice to generate strain while maintaining morphology. More importantly, some nanostructures, such as metastable phases, are usually unstable during catalytic reactions, and the dissolution of atoms from the lattice during catalysis resulting in the disappearance of the strain effect is also an urgent problem to be solved. For the future



development of Pd-nonmetal nanocatalysts, efforts could be devoted to the following aspects (Fig. 7). First, it is suggested to develop more Pd-nonmetal nanostructures, especially for Pd-S, Pd-Se, Pd-Te, and Pd-P, which have rich phases. Second, efforts could be devoted to developing more amorphous Pd-nonmetal nanostructures that may serve as highly active and durable nanocatalysts. Third, the coalloying of two nonmetals with Pd deserves more attention, which may produce unexpected catalytic performance.

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Author contributions

M.J.W. and L.G.L. contributed equally to this review, conceived the theme, and wrote the manuscript. M.M.W. designed the layouts of Fig. 1 and edited the references. X.Q.H. proposed the topic of the review.

Competing interests

The authors declare no competing interests.

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