Strain modulation of phase transformation of noble metal nanomaterials

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Abstract
Noble metals have been extensively studied owing to their high chemical stability and outstanding catalytic properties in various important reactions. However, their large-scale application of noble metals is still challenged by their high expense and scarcity on the earth, as well as the yet insufficient activity to give a satisfying performance. For decades, enormous research efforts have been devoted to the nanoengineering of noble metal nanocrystals, such as the size-, composition-, shape-, and/or morphology-controlled syntheses, and impressive advances have been achieved. Meanwhile, the discovery that the crystal structure of noble metal nanocrystals also has a significant impact on their properties opened a new pathway that modulates the crystal phases of noble metals to achieve better properties. Among the feasible methods for crystal phase transformation, the presence of strain is not negligible. Strain generally has two roles: the driving force of the phase transformation and/or the origin of the distinct properties of the new crystal structure. Strain effect on noble metals has also been extensively studied due to its capability of fine-tuning the surface catalytic activity. Therefore, combining the two hot research trends together, a possible research pathway is emerging. That is, utilizing the potential synergistic effect between novel crystal phases and the subsequent lattice strain to boost the performance of noble metal nanocrystal even further. Herein, a brief summary of the currently discovered noble metal phases and strain effect and the introduction of strain related phase modulation techniques along with the catalytic applications will be presented. Finally, a brief conclusion and future perspective is given.

KEYWORDS
nanocrystal, noble metal, phase modulation, strain effect

1 | INTRODUCTION

Noble metals have raised enormous research interest due to their superior resistance to corrosion while being highly active in catalysis of many reactions. For instance, Pt has been widely known as the most efficient catalysts for electrochemical reactions such as hydrogen evolution reaction (HER), and oxygen reduction reaction (ORR).
while Ru and Ir and their alloys present the most promising activity toward oxygen evolution reaction (OER).\textsuperscript{1–3} Nevertheless, the application of noble metals, especially those for commercial and large-scale usage, is limited by the yet insufficient activity and high expense of the noble metal materials themselves. Therefore, armed with powerful nanoengineering techniques, scientists exploit the potential of noble metals by synthesizing various kinds of nanomaterials consisting of noble metals. Through rational design and controlled synthesis, size, shape, and compositions of nanomaterials can be engineered to produce materials with desired properties for specific applications. The crystal phase engineering of noble metal did not receive much interest until recently, since noble metals normally crystallize into the closest-packed structure in bulk, like face-centered cubic (fcc) or hexagonal close-packed (hcp), under ambient conditions.\textsuperscript{4} However, when it comes to nanoscale, the dominant factor of system stability becomes the surface energy instead of the total system energy.\textsuperscript{5} Therefore, phases other than fcc and hcp can be stably presented in the nano noble metal materials under ambient condition. Besides the size effect in nanoscale, these phases can also be stabilized by considering surface/internal stress, surfactants, growth templates, and precursors in the synthesis process.

The nanomaterial phase modulation is of profound research interest due to its ability to tune the properties of nanomaterials. The crystal phase affects the shape and exposed facets of nanoparticles, while the stacking pattern of atoms could also modify the electronic structure. Therefore, crystal phase modulation can tune properties that are affected by these geometric and electronic factors. The currently reported and discussed phase-dependent properties include optical, electrical, catalytic, and magnetic properties. Previous studies compared the optical properties of 4H-Ag and fcc-Ag and also the 4H-Au and fcc-Au, respectively.\textsuperscript{5} The results demonstrated the effect of phase change in various optical properties, such as the absorption range in UV-vis spectrum, the vibration modes in Raman spectra and the shift of SPR peaks in EELS spectra. Electrical conductivity and electrical noise have been demonstrated to be phase-dependent in the researches on Ag and Ni nanoparticles.\textsuperscript{7–8} The impact of phase modulation on catalytic properties is more explicit, as changes in phase affect the geometry of surface as well as the electronic structure, both of which play a significant role in catalytic reactions. For instance, the face-centered-tetragonal (fct) FePt@Pt core-shell nanoparticles demonstrate a higher ORR activity than that of the fcc counterparts.\textsuperscript{9,10} The distortion of tetragonal modifies the lattice strain of the surface Pt layer to adjust the adsorption strength of oxygenated species to the optimal value, and thus the activity is enhanced. These cases clearly suggest the crystal phase of nanomaterials has a remarkable effect on the intrinsic reactivity. In addition, a distinct reaction path may also emerge due to the change of the crystal phase, leading to a potentially better catalytic activity. It is noteworthy that the study on phase-dependent properties is still at an early stage. Therefore, the potential of phase modulation on tuning nanomaterial properties is still large and it embraces more research interests.

Strain is a quantitative descriptor of the structural deformations in geometry in the response of the applied stress on the system. It is generally evaluated by the change of lattice parameters:

\[ \text{strain} = \frac{l - l_0}{l_0} \times 100\% \]

where \( l \) and \( l_0 \) are the strained lattice parameter and unstrained lattice parameter, respectively, and \( l_0 \) is determined from the unstrained bulk lattice constant.\textsuperscript{11} The strain on crystal structures inevitably induces changes in the packing patterns, interatomic interaction, displacements, and potential defects in the crystals. As a result, properties related to these features will be affected by the strain. Moreover, the geometric effects brought by the strain would induce a significant impact on the densely packed nanocrystals because the chemical bonding mode varies with the packing mode, which change the thermodynamic stability order of the possible crystal phases. In this manner, modulation of strain becomes a capable tool of crystal phase transformation and can be specifically accomplished via various methods, which will be introduced in the following sections.

Catalytic activity tuning via strain has been a hot research topic in recent years. The strain-induced activity tuning is a phenomenon combining geometry effect and electronic effect together. Namely, the lattice strain in crystals affects the interatomic distance, which subsequently affects the orbital overlaps and hence the electronic band feature is changed. For instance, the d-band of transition metals will be broadened by compressive strain while sharpened by tensile strain. As the lattice strain normally has no direct impact in the electron-fillings in the d-band, if the band widens, it must move down in energy to maintain the constant d-band occupancy. Conversely, if the band sharpens, it must move up in energy to conserve the d-band filling.\textsuperscript{12} The change of d-band energy is depicted by the widely accepted d-band center theory model.\textsuperscript{13} The shift of surface d-band center relative to the Fermi level is found to correlate with the adsorption strength of species on this surface.\textsuperscript{1} Moreover, on the basis of Sabatier principle, there is a volcano plot in which the optimal catalytic activity locates in a moderate adsorption strength, neither too strong nor too low. Therefore, strain is capable of fine-tuning of surface reactivity.
and it has been applied and studied extensively in the development of novel electrocatalysts. However, the major of the strain study only investigate the lattice strain induced from lattice mismatch of core-shell structures and externally applied strain, while little attention is paid to the intrinsic strain of modulated phases and distorted structures. For this reason, the strain effect in the phase-modulated noble metal nanocrystals and its impact on catalytic properties will be introduced in this work.

Herein, the background knowledge of crystal phases of noble metal nanocrystals will be briefly discussed, and then the major strain modulation techniques for phase transformation will be gone through with documented studies provided. The applications of these phase-transformed nanomaterials will be discussed to demonstrate the merits of the phase transformation. Finally, we will summarize the current challenges in strain modulation phase transformation for the noble metal nanomaterials, and remark on the future development.

## 2 Crystal Phases of Noble Metal Nanomaterials

Noble metal nanocrystals, usually adopt the common fcc structure which is the thermodynamically most stable phase in ambient condition, except the cases that Ru and Os adopt hcp structure. The fcc and hcp are both the close-packed structures with the highest atomic packing factor of 0.74, and they have the same atomic arrangements in the close-packed planes. The essential difference between hcp and fcc is the stacking sequence of the close-packed planes. The fcc is stacked along the [111] direction with a sequence of ABC, whereas hcp is stacked along the [100] direction with a sequence of AB. The fcc and hcp structures can be also noted as 3C and 2H structures, respectively, where the numbers represent the number of planes in a packing period, “C” represents the cubic Bravais lattice and “H” represents hexagonal Bravais lattice. Besides the fcc and hcp phases, it has been shown that noble metal nanocrystals can also crystallize into a variety of other structures, including the 4H hexagonal phase, face-centered trigonal phase, and body-centered tetragonal phases, which have been found in nanocrystal of noble metals such as Au and Ag. The normal and chemically derivable phases are summarized in Table 1.

### 3 Strain-Assisted Phase Modulation Techniques

The rapid development of the phase transformation techniques enable the synthesis of catalysts with more complex crystal structures or surface configurations. Strain has been found to be an important driving force in facilitating the phase transformation process of noble metal nanocrystals. In particular, the strain can be introduced into the materials either directly or indirectly. For instance, the application of external pressure is a direct method to induce strain in the crystals. Indirect introduction of strain frequently follows with the surface modification of materials or generation of crystal defects. In the following sections, four major strain-assisted phase transformation techniques will be introduced. A summary of the techniques, examples, and applications in electrocatalysis is given in Table 2. The mechanisms and the role of strain will be illustrated with specific examples.

### 3.1 External pressure driven phase modulation

Direct application of pressure externally on the nanocrystals is an explicit method to force the crystal to deform to other structures or shapes. During the deformation process, the lattice will be inevitably strained in response to the applied pressure. Therefore, the external high-pressure-induced phase transformation method can be also considered as strain related and hence it will be discussed herein. The pressure-induced transformation method is widely used in the crystal phase transformation of a variety of materials, including metals, semiconductors, nanotubes, perovskites, and even heterostructures. The diamond anvil cell (DAC) is an equipment that is capable of generating homogeneous pressures around 100 to 200 GPa easily and even higher. To obtain a good high-pressure experiment result, the distribution of pressure should be homogenous on the sample, which indicates the hydrostatic nature of the sample to guarantee the uniform compressibility throughout the sample (see Figure 1A). It is therefore predominantly used to perform the pressurization on the materials. Along with the pressurization in DAC, synchrotron X-ray diffraction is usually used for direct in situ observation of crystal phase transformation. The critical pressures for phase transformation of noble metals in bulk are generally quite high and the conditions

| Noble metal | Bulk phase | Unique crystal phases |
|-------------|------------|-----------------------|
| Ag          | fcc        | 4H, 5,18,21 2H, 24 fcc, 22 trigonal, 20 bct 19 |
| Au          | fcc        | 4H, 23,24 2H, 6,25-27 bct, 28 bco 26 |
| Pd          | fcc        | fcc 29 |
| Ru          | hcp        | fcc 30-35 |
| Rh          | fcc        | Single layer, 36 2H 37 |

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**Table 1** Summary of the reported crystal phases of noble metal nanocrystals
are harsh. For instance, the required pressures for noble metals to transform from fcc phases into other phases are 77.4, 304, 91.8, and 182 GPa for Pd, Pt, Ag, and Au, respectively. This is because the noble metals tend to crystallize into the closest-packed structures (fcc or hcp) under ambient conditions as they are thermodynamically most stable in these phases. The phase transformation of noble metals in bulk thus becomes very difficult to proceed. However, when the size is reduced to nanoscale the threshold pressure for phase transformation and structural distortion is substantially decreased to a relatively ambient level. The mechanism behind is the dominant factor deciding the system stability changes from the internal volume energy to the surface energy when the particle size is reduced to the nanoscale. Still, the pressure for the crystal phase transition is related to the size and morphology of the nanocrystals and even the surface capping organic layers. An interpretation from electronic structure reports that for noble metals the phase transition of hcp to fcc is contributed by increasing s-p mixing of valence states and partial-valence states of 5d states, while the transition from fcc to body-centered tetragonal (bct) phase is assumed to occur due to the enhancement of sp-d mixing states at valence bands with the increasing pressure. However, the crystal phase transformation induced by pressure is conventionally reversible, which is not desirable for further studies of physicochemical properties and practical applications of the high-pressure-induced crystal phases.

Pressure-induced phase transformation methods have been successfully adopted in several cases of noble metal nanocrystals. The fcc to fct phase transformation in Pd nanocubes with an average side length of ~10 nm under pressure up to 24.8 GPa has been reported by Guo et al. Based on their experimental results, they proposed a mechanism that the nanocrystals in DAC is uniaxially compressed along the [001] direction and they predicted that a similar fcc to fct distortion might be observed in cold-compressed Pt, Ag, and Au nanocubes with [100] as the exposed crystal faces. A study on Ag nanoparticles by K.J.Koski et al presented experimental evidence of the reversible structural transformation under hydrostatic

| Strain application | Techniques | Phase modulation effectiveness | Material | Phase | Catalyzed reaction | References |
|--------------------|------------|-----------------------------|----------|-------|-------------------|------------|
| Direct             | External pressure | Low, rarely irreversible | Pd, Pt, Ag, and Au | fcc to fct | Not reported | Guo et al 29 |
|                    |             |                             | Ag      | fcc to distorted trigonal | Not reported | Guo et al 20 |
|                    |             |                             |         | fcc to rhombohedral | Not reported | Sun et al 22 |
|                    |             |                             |         | 4H to 3C | Not reported | Chakraborty et al 21 |
| Indirect           | Template-mediated growth | High, controllable | Au nanoribbon | 4H to fcc | Not reported | Li et al 23 |
|                    |             |                             | Au@PdAg core-shell NRB | 4H/fcc | HER | Fan et al 38 |
|                    |             |                             | Pt@Ru tetrahedrons/C | fcc | HOR | Gu et al 39 |
|                    |             |                             | PdFe@Pd core-shell | fct | ORR | Maiti et al 40 |
|                    |             |                             | Au@M (M = Ir, Os, IrOs) core-shell NRB | 4H/fcc | OER | Fan et al 41 |
|                    |             |                             | Au-Ru nanowire (NW) | 4H/fcc | alkaline HER | Lu et al 42 |
|                    |             |                             | Au square sheets | hcp to fcc | Not reported | Fan et al 24 |
|                    |             |                             | Au NRB | 4H | Not reported | Fan et al 46 |
|                    |             |                             | Ag NW | bct | Not reported | Sun et al 19 |

Abbreviations: HER, hydrogen evolution reaction; NRB, nanoribbon; OER, oxygen evolution reaction; ORR, oxygen reduction reaction.
pressures up to 10 GPa, with the Ag nanoparticle size ranged from 5 to 10 nm. Ag nanocrystals have also been transformed from fcc to a distorted trigonal structure, the fcc to rhombohedral structure, and 4H to 3C structure reported by literatures. Anmin Nie et al observed an fcc to bct transformation during in situ tension of gold nanocrystals in conjunction with transmission electron microscope and validated the MD simulation prediction. Mendoza-Cruz
et al. reported an orthorhombic lattice distortion in single-crystal truncated-octahedral gold nanoparticles under a pressure below 12 GPa in the DAC cell at room temperature (295 K).43 Such an ambient condition for Au lattice deformation is impossible for Au in bulk, demonstrating the significance of size effect. The atomic resolution electron microscopy and electron diffraction results detected an asymmetrical lattice distortion of ~3% along the lattice planes, which indicated the cubic to orthorhombic structural transformation originated from the lattice strain generated by the aforementioned experimental conditions. They also observed that this lattice distortion did not occur to the twinned nanoparticles of Au subjected to the same pressure and temperature conditions, indicating that this lattice distortion should be dependent on the particle structure and morphology along with the size effect. These studies above substantially demonstrate the possibility of phase transformation of noble metal in nanoscale.

It is worthy to note that an irreversible pressure-induced phase transformation from 4H to fcc phase of Au nanoribbons has been reported, which contradicts the conventional perspectives and theories that the pressure-induced phase transformation of noble metal should be reversible.23 XRD diffraction patterns demonstrated the shrinkage of the crystal lattice. When the pressure is built up, the intensities of 4H diffraction peaks decrease while the intensities of fcc diffraction peaks increase, revealing the transformation is a gradual process. More importantly, the relative quantity of fcc phases formed by pressure remains unchanged after decompression, demonstrating the stability of the pressure-induced fcc phase and the irreversible nature of this 4H to fcc transformation. In order to interpret this contradiction to the traditional pressure-induced phase transformation theory, they proposed a mechanism that the atoms directly shift from the (112) facets of 4H Au to the nearest face centers of four nearest Au atoms in the ac plane, rather than following the conventional mechanism that it is the partial dislocations on the close-packed surface planes that generate the new crystal phase (Figure 1C-F).23 The further thermodynamic calculation with enthalpy as a function of pressure provides theoretical proof that the transformation from 4H to fcc is mediated by the atomic motion mechanism.

The pressure-induced transformation method is a widely adopted method in the attempts of achieving phase transitions in noble metal nanocrystals, owing to the simple experimental procedures and powerful in situ characterization techniques that can track the phase changes during the variation of pressure. Therefore, there have been many documented studies on the successful application of this technique. However, since the phase transformation in this approach is reversible in general, the practical applications of the pressure-induced phase-transformed nanocrystals and further research on their properties are limited. The reservation of the transformed phase after the removal of external pressure or auxiliary postprocessing of the nanocrystals should be further developed and investigated to solve this important issue.

### 3.2 Template-mediated growth method

Template-mediated growth method, which can be also called as epitaxy method, features a strong geometric effect on the crystal overgrowth and is an effective approach to synthesize noble metal nanocrystals with unique phases.51 Epitaxy refers to the deposition process of an overlayer on a crystalline substrate which works as a template for the growth of the overlayer. Usually, there is a subtle difference in the crystal structure of the substrate template and the growing layer, which is the origin of the lattice mismatch between the two components. The lattice mismatch inevitably deforms the structures of the growing layer and thereby, strain exists in the system. Depending on the extent of the lattice mismatch between the overlayer and the substrate and the subsequent strain effects, the epitaxy process is generally subdivided into epitaxial growth and non-epitaxial growth. Epitaxial growth takes place when the lattice mismatch and strain effect is fairly small. In this case, the lattice mismatch and strain effect together act as a constraint in the geometry of the as-formed metal crystal structure and growth mode. Therefore, the subtle strain in the epitaxial growth process generally assures that the growth layer has the same phase as the template. In this manner, new noble metal nanocrystals with desired phases can be obtained by selecting the proper seeds with the target phase and similar lattice parameters. For instance, the unusual 4H hexagonal Ir, Rh, Os, Ru, and Cu nanostructures are synthesized on a 4H Au nanoribbons via solution-phase epitaxial growth under ambient conditions, obtaining a series of Au@M (M = Ir, Rh, Os, Ru, and Cu) core-shell nanoribbons (Figure 2A).54 Moreover, the 4H/fcc trimetallic shells can also be synthesized using the 4H/fcc-Au@Ag nanoribbons.38 In recent years, the epitaxial growth of hybrid noble metal nanostructures has been further developed. Lu et al. proposed a crystal phase-based synthesis strategy of epitaxial growth of Ru nanorods on 4H/fcc-Au nanowire and it could be extended to the synthesis of trimetallic hybrid nanowire on the Au-Ru nanowire, which is obtained from this method, as the seed for the epitaxial growth process.42 A typical epitaxial growth of noble metal crystals begins with the proper selection of metal nanocrystal seeds, followed by the successive epitaxial depositions,55-57 or Galvanic replacement reactions.58 with a secondary noble metal.
On the other hand, when the lattice mismatch and strain between the substrate are large to an extent, the subtle constraint from the chemical bonds in the interface is replaced by the substantial strain on the structure. In this case, the crystal growth becomes the non-epitaxial kind. The structure of the growing layer will adopt distinct structures from the substrate depending on the types and magnitude of the strain. Therefore, the tendency of epitaxial growth and non-epitaxial growth is adjustable when the magnitude of the lattice mismatch is tunable. A convenient way to control the lattice parameters is by forming an alloy with different chemical compositions. Tuning the lattice parameters of the growing template enables the indirect control of strain on the
growing layer to undergo epitaxial growth or non-epitaxial growth, depending on the targeted phase for the product. Take the Ru growth on PdCu nanocrystals as example, fcc Ru can grow when the lattice mismatch between the PdCu alloy and Ru is small while hcp Ru is formed when the lattice mismatch is sufficient enough to create a large strain, and thereby the Ru seeks the global energy minimum geometry structure, the hcp phase (Figure 2B-D). Additionally, there are methods that apply strain externally during the growth process to turn it from epitaxial growth to non-epitaxial growth. An example is that during the growth of Au on a fcc-Au nanorod, organic ligands are introduced onto the surface of Au nanorods to artificially create a shear strain, which largely enhances the lattice mismatch between the Au growing layer and the underlying Au nanorod surface. The final product of this process is a multiply twinned overgrown Au nanostructure.

Besides the utilization of metallic crystal substrate as the template for the epitaxy process, using nonmetallic substrates is also viable for the growth of noble metal nanocrystals. Graphene oxide (GO), oxidized from the substrates is also viable for the growth of noble metal nanocrystals. Graphene oxide (GO), oxidized from the substrates is also viable for the growth of noble metal nanocrystals. The final product of this process is a multiply twinned overgrown Au nanostructure.

In summary, the template-mediated growth method utilizes the lattice mismatch between the template and growing layer and the subsequently produced strain between the interface to achieve a crystal phase-controllable synthesis for noble metal nanocrystals. The two distinct pathways of template-mediated growth method, epitaxial growth and non-epitaxial growth, can be switched between each other by finely tuning the lattice mismatch. Methods for controlling the lattice mismatch involves selecting a template with similar element and phases or synthesizing alloy with varying chemical compositions to control the lattice parameters of the template. Meanwhile, surface ligand decoration on the metallic template for the epitaxy process, using nonmetallic substrates is also a viable method to control the epitaxial or non-epitaxial growth process.

3.3 Strain-induced phase modulation by surface ligand

Surface energy has been widely recognized as the dominant factor of the total energy of nanoscale systems and the key factor for the formation of new crystal phases which are not stable in bulk. Therefore, approaches that can modulate and stabilize the surface energy enable the phase transformation or formation of new phases for noble metal nanocrystals. Adsorption of surface ligands is one of the approaches that meet the criteria above, as the adsorption of ligand to the surface will induce multiple changes in the structure geometry, electronic structure of the nanocrystals and possibly other properties of the system. Moreover, the adsorption of ligands will induce strain on the adsorption sites, which might deform the structure to some extent and thereby change the surface energy. A typical example of ligand used in the synthesis of noble metal nanocrystals is the thiol ligand. The thiol ligand has been proven to be an effective tool to break the symmetric growth of metallic nanocrystals and induce surface reconstruction of metals.

They investigated the asymmetric monometallic Au nanorod-Au nanoparticle dimer nanocrystals and identified the growth pathway with TEM (Figure 3A-F). It is concluded that the thiol ligands exert the effect in both thermodynamics and kinetics. In thermodynamics, the thiol ligand induces significant and inhomogeneous surface strain on the Au nanorod and stacking faults for the growth of Au nanoparticles. Meanwhile, kinetically, it regulates the reduction rate of Au precursor to prevent uncontrolled deposition of the Au nanoparticles.

Feng et al also investigated the unconventional role of the ligand in continuously tuning of metal-metal interfacial strain. They observed that adjusting the 2-mercaptobenzoi-imidazole-5-carboxylic acid (MBIA) ligand conditions alone is able to continuously change the growth mode of Ag-Ag dimer. The following investigation reveals that the strongly bound ligands on the newly grown Ag surface force the subsequent Ag growth into islands. The lattice mismatch factor is excluded since both the substrate and the grown layer is Ag, and hence the only origin of the strain is from the binding of MBIA ligands. Subsequent experiments with varying ligand concentration unwrap that at high ligand concentrations, there will be an organic defect in the ligand layers. Such defects will introduce strain in the metal lattices and making a significant impact on the interfacial energy. Thus, the growth
mode of Ag has to adapt to the strain-induced interfacial energy changes and endeavor to minimize the interfacial energy. The role of ligand that can induce strain for surface reconstruction has also been applied in the phase transformation from hcp to fcc structure of Au square sheets (AuSS), reported by Fan et al.²⁴ The adsorbed thiol molecules will induce a (100)₉ surface reconstruction, which initiates a complete phase transition over its entire structure. Moreover, accordingly, the choice of surface ligand used for the metal coating process will lead to two phase transformation product of Au@Ag nanosheets. Fan et al also reported that the surface coating ligand exchange facilitates the 4H-fcc phase transformation of Au nanoribbon (AuNRB) under ambient conditions (Figure 3G).⁶ In summary, the strong interaction between ligand and metal surface will induce surface strain and the subsequent surface reconstruction. Therefore, ligand exchange is an effective method in phase engineering of noble metal nanocrystals, and strain is the major driving force during this process.

3.4 Internal defects induced strain phase modulation

The source of strain on the lattice is not limited to the external factors, like the lattice mismatch between substrate and crystal or directly applied mechanical forces. The intrinsic defects of crystal, involving stacking faults, twins, grain boundaries, and/or dislocation arrays, would also deform the ordered crystal structure and induce various magnitude of strain on the crystal lattice.⁶⁸ Therefore, artificially creation of such crystal defects during the synthesis of noble metal nanocrystals is another means of nanocrystal phase transformation or modulation.

Twins, along with stacking faults, are the typical crystal defects which are readily formed during the growth of crystals with low stacking fault energy.⁶⁹ for instance, Au and Ag. In the growth of crystal, the atoms may erroneously attach to the growing crystal and behave as an intergrowth of two separate crystals (Figure 4C-E).⁷⁰ The fivefold
twinning structure is a very intriguing microstructure because it has been demonstrated that for small nanoparticles, the equilibrium shape predicted by the Wulff theory is not exclusively observed but also with the multi-twinned nanoparticles, especially with those with fivefold symmetry. The fivefold symmetry shape consists of five tetrahedrons bounded by \{111\} facets joining together. The theoretical angle between two (111) planes is $70.52^\circ$, so there is a gap of $7.40^\circ$ when the five tetrahedrons are joined (Figure 4B). Therefore, to fill the gap in space, the internal strain is required to force the components together, leading to dislocations and other structural defects. The extra energy derived from the internal strain, stacking faults and angle gap is needed to compensate, which creates the possibility of structural and phase transformation of the nanocrystals. A non-fcc phase noble metal nanomaterial example is the \textit{bct} phase in Ag nanowires reported by Sun et al (Figure 4A).\textsuperscript{19} It has been predicted by molecular dynamics simulations that the \textit{bct} phase of Ag and other metals is possible from a spontaneous phase transition of very thin \textit{fcc} nanowires (diameters <2 nm) owing to very high surface stresses in the nanowires.\textsuperscript{71-73}\textsuperscript{71-73} The \textit{bct} phase also possibly exists in slightly thicker nanowires (diameters <5 nm) by applying external high pressures to the nanowires.\textsuperscript{22} For Au, similar thickness-induced phase transformation has also been observed in ultrathin gold films and wires with a lateral dimension smaller than 2 nm.\textsuperscript{27,74}\textsuperscript{27,74} Although \textit{bct} phase nanowire of Ag with a diameter smaller than 2 nm is also predicted to be possible by MD simulation, it is much more difficult to synthesize it in the experiment due to the high surface energy and structural instability. On the other hand, Ag nanoplates with multiple parallel twin planes have been observed to have a \textit{fcc} to \textit{bct} phase transition under external pressures higher than 12 GPa, while the Ag nanocubes without internal crystalline defects remain perfect \textit{fcc} at even higher pressure.\textsuperscript{22} These results inspired Sun et al to apply the internal crystalline defect control strategy to synthesize tetragonal phase nanoparticles of large lateral dimensions.

**FIGURE 4**  A, SEM image of Ag nanowires randomly assembled on the surface of a silicon wafer. The upper right inset of (A) is the TEM image of the cross section, which is viewed parallel to the longitudinal axis of the nanowire. The scale bar in (A) represents 500 nm. B, Schematic drawing of the fivefold twinned Ag nanowire and the illustration of the angle gap.\textsuperscript{19} Reprinted with permission. Copyright 2012 Springer Nature Limited. C-E, Examples of contact twinning in small particles: (C) silver nanoparticle particle with a single twin, (D) gold nanoparticle with lamellar twins, and (E) decahedral gold nanoparticle (cyclic twinning).\textsuperscript{70} Reprinted with permission. Copyright 2006, the Royal Society of Chemistry
dimensions even at ambient pressure. The bct phase in the Ag nanowires synthesized by Sun et al is formed as a result of the distortion of cubic lattice owing to the internal strains in the twinned nanoparticles.\textsuperscript{19} The internal strains originated from the fivefold twinning boundaries concentrates in the central region, creating a tetragonal distortion of the nanoparticles. Meanwhile, further analysis reveals that there are lattice defects including stacking faults, partial dislocations, slips and possible additional small crystal domains in the central region to alleviate the strong internal strain and stabilize the phase. On the other hand, the surface is free of defects, except the \{111\} twinning plane, suggesting the surface regions experience less strain than the central regions. These results altogether indicate that the Ag nanowire is a core/shell structure with a highly strained core due to the twinning planes and a less strain shell to protect the core. Furthermore, such bct phase is also observed in decahedral Ag nanoparticles with the same fivefold twinning structure, which further proves that the fivefold twinning structure is able to generate large lattice distortion and strain for the tetragonal deformation and \textit{fcc} to bct phase transition in noble metal nanoparticles.

The potential of utilization of internal defects, especially the twins and stacking faults, remains to be further investigated and developed. There have been several molecular dynamics simulations on the growth of noble metal nanocrystals addressing the role of twins and induced-strain in the control of phase of the product nanocrystals\textsuperscript{\textsuperscript{71-73,75,76}} and they have predicted the possible existence of bct and bco phases in the growth nanocrystals with such fivefold twinning structures. Although the internal strain induced by this twinning defect increases simultaneously with the particle sizes, which makes the preparation of fivefold twinning structure noble metal nanocrystals very strict with the particle size control, it has been reported that a fivefold twinning bipyramidal Au microcrystal with ambient stable tetragonal and orthorhombic phases is successfully synthesized.\textsuperscript{28} The success in the theoretically difficult synthesis of the twinning structure at a much larger scale should inspire material scientists to adopt the strategy on other noble metals, such as Cu, Pd, Pt, and Ru to develop noble metal nanocrystals with non-\textit{fcc} phases.

\section{Catalytic Performance of the Phase-Modulated Noble Metal Nanocrystals}

The catalytic properties of nanocrystals are greatly affected by their crystal phases since crystal phase determines the stacking mode of the atoms, the exposed surface of the crystal, coordination environment of the atoms. These geometric effects in turn impact the electronic structure of the atoms in the nanocrystals as the interatomic interaction is affected. Therefore, the variation of phase would have a significant effect on the activity and selectivity of the active sites, as well as the active site density.\textsuperscript{77,78} For example, strain modulation has been widely used in many transition metal electrocatalysts to fine-tune the catalytic activity.\textsuperscript{11,78-80} The catalytic activity of the surface is adjusted due to a series of synergy change on geometric and electronic factors, for instance, shift of d-band center under tensile or compressive strain, and reflected in the adsorption strength of adsorbates, which is a well-established descriptor for the electrocatalytic activity of a material.\textsuperscript{1} In addition, not only the catalytic activity but also the catalytic durability can be remarkably enhanced.\textsuperscript{10} Therefore, upon the change of phase, multiple properties that are dependent on the geometric and electronic factors may display diverse performance compared to the nanocrystal with the original phase. As the phase transformation has just grasped the focus in the research community, the study of phase-dependent properties is still at an early stage limited by the yet premature synthesis method of phase-transformed nanocrystals. Herein, the applications of phase-modulated noble metal nanocatalysts in four fundamental energy conversion related reactions will be reviewed, with emphasis on how phase modulation and strain affect the catalytic activity of the materials.

\subsection{Hydrogen evolution reaction}

The environmental issues have been a globally concerned topic as there is a growing awareness of sustainability around the world. Hydrogen, which is easily obtained from the water by HER, is considered as a clean, efficient, and abundant sustainable energy resources.\textsuperscript{81,82} The production of hydrogen through HER and solar energy is a promising pathway, especially with the employment of catalysts consisting of noble metals. Despite their excellent activity in HER, the scarcity and high cost of noble metal limit their practical large-scale application in HER. Numerous noble metal nanocatalysts for HER have been designed, synthesized, and studied extensively to further improve the catalytic efficiency and in the meantime reduce the usage of noble metal so that the balance between performance and expense can be reached. A recently emerging study interest is the crystal phase modulation of the noble metal nanomaterials since researches have shown that the catalytic activity is correlated to their crystal structure.\textsuperscript{10,83} Consequently, potential high catalytic activity noble metal nanocatalysts could be obtained with phase modulation methods.

A polytypic 4H/\textit{fcc}-Au@PdAg core-shell nanoribbon (NRB) synthesized by epitaxial growth by Fan et al is
reported to exhibit excellent catalytic activity and remarkable durability toward HER. The onset potential and overpotential (at 10 mA/cm²) are 2.0 and 26.2 mV, respectively, which are dramatically lower than the commercial Pd black (onset potential: 85.0 mV; overpotential: 135.6 mV) and close to those of the commercial Pt black (onset potential: 0.5 mV; overpotential: 16.5 mV; Figure 5A,B). The Tafel slope of Au@PdAg nanoribbon is quite low (29 mV/decade) and very close to that of commercial Pt black (27 mV/decade; Figure 5C). In the durability test, the Au@PdAg nanoribbon retained the activity even after 10 000 potential cycles. The robustness of this 4H/fcc-Au@PdAg nanoribbons should allow its application in harsh environmental conditions. The greatly enhanced activity and durability can be ascribed to the unique 4H/fcc crystal structures as well as the unique surface morphology that is rich with atomic steps and kinks (Figure 5I).

Pt-Ni alloy typically crystallizes into the fcc structures. In spite of that, with a facile one-pot solvothermal route, a hcp phase Pt-Ni alloy nano-multipods are synthesized and exhibit superior catalytic property toward HER in alkaline condition. The hcp Pt-Ni excavated nano-multipods possess a new crystal phase, low Pt content, and high surface area owing to the excavated polyhedral shape (Figure 5J). It is expected to be a low-cost catalyst.

**FIGURE 5** The improved HER activity of phase-modulated noble metal nanoparticles. A-C, The polarization curves, onset potentials, and overpotentials (at 10.0 mA/cm²), Tafel plots of 4H/fcc-Au@PdAg NRBS, Pd black, and Pt black. D, Durability test of 4H/fcc-Au@PdAg NRBS. Reprinted with permission. Copyright 2016 American Chemical Society. E and F, HER polarization curves of three catalysts in 0.1 M KOH normalized by (E) ECSA and (F) mass of Pt. G, Measured HER kinetic current densities (scatter dots) and their fittings based on the Butler-Volmer equation (dotted line). H, Arrhenius plots of the HER exchange current densities. Reprinted with permission. Copyright 2017 Springer Nature Limited. I, Schematic illustration of the synthesis of 4H/fcc noble multimetallic nanoribbons. Reprinted with permission. Copyright 2016 American Chemical Society. J, Schematic illustration of the formation of excavated Pt-Ni multipods. Reprinted with permission. Copyright 2017 Springer Nature Limited. HER, hydrogen evolution reaction; NRB, nanoribbon
for large-scale practical applications. The HER performance is measured together with the fcc counterpart transformed from the synthesized hcp Pt-Ni excavated nano-multipods (with the composition and morphology almost unchanged) and commercial Pt/C as reference. The hcp Pt-Ni excavated nano-multipods showed superior performance with the much smaller overpotential and multiple times of current densities at the potential of 70 mV vs RHE compared to the fcc counterpart and commercial Pt/C (Figure 5E,F). Further investigation of catalytic mechanism reveals that the hcp and fcc Pt-Ni alloys possess similar Tafel slope (78 mV dec⁻¹ and 74 mV dec⁻¹) while both being less than the one of commercial Pt/C (117 mV dec⁻¹; Figure 5G). The lower Tafel slopes in both Pt-Ni alloy indicate the formation of Pt-Ni alloy facilitates the HER in alkaline condition. The similar Tafel slopes demonstrate that the two catalysts undergo similar reaction pathways. However, the exchange current density of the hcp Pt-Ni alloy is 1.00 mA/cm² larger than those of fcc Pt-Ni alloy and commercial Pt/C. Moreover, the activation energy of hcp Pt-Ni alloy was measured to be also smaller than that of fcc counterpart and the commercial Pt/C (Figure 5H). Finally, the durability test of hcp and fcc Pt-Ni alloy and commercial Pt/C demonstrates that despite the fact that current density of hcp Pt-Ni alloy dropped a bit in a few moments at the beginning, the overall and steady current density was much higher than those of the fcc counterpart and the commercial Pt/C. Therefore, the hcp Pt-Ni excavated nano-multipods exhibits the best HER activity among the three tested catalysts, and this activity enhancement should mainly attribute to the modified phase and surface morphology of the materials. In addition, an Au-Ru hybrid nanowire synthesized by an epitaxial growth of Ru nanorods on 4H/fcc-Au nanowires also exhibit superior HER activity in alkaline medium to the conventional Pt/C, Ru/C, and other reported electrocatalysts. In conclusion, the significance of phase modulation of noble metal nanocrystals is profound, which may offer new pathways and opportunities for developing more efficient noble metal catalysts for HER reaction.

### 4.2 Hydrogen oxidation reaction

Hydrogen oxidation reaction is the half-reaction that the hydrogen being oxidized to protons in the anode of proton exchange membrane fuel cells or subsequently turned to water molecules in alkaline fuel cell systems. Fuel cells are expected to replace fossil fuel engines in the future because fuel cells feature higher energy conversion efficiency, theoretically zero pollution and abundant as well as a sustainable energy source. Nevertheless, the development of fuel cells, especially for the alkaline fuel cell systems, is limited by the yet to be improved rate of HOR. Noble metal nanocrystals are also the capable candidates for catalysis of HOR, especially Pt- and Ru-based nanostructures, which possess high catalytic activity toward HOR. Phase modulation has been successfully implemented on several noble metal nanocrystals to synthesize catalysts with frequently superior activity in HOR compared to their normal phase counterparts and the benchmark commercial Pt/C. Gu et al found an enhancement in acidic HOR activity with more than an order of magnitude in fcc Pt@Ru tetrahedrons/C catalysts compared with the normally synthesized hcp Ru/C (Figure 6A-F). A robust phase control strategy utilizing epitaxial growth and hydrothermal method was developed and implemented in the synthesis of M@Ru (M = Pt, Pd) nanocrystals in the fcc phase, which is a metastable phase for Ru under ambient conditions. The Pt@Ru nanocrystals featured a pure fcc phase as well as a high morphology selectivity to tetrahedrons surrounded by [111] facets. Density functional theory (DFT) calculation revealed that the formation of stable fcc Ru shells was ascribed to the epitaxial growth of Ru layers on the nonclosest-packed facets of hetero fcc metal seeds. Electrochemical measurement and DFT calculation results unraveled and emphasized that the well-crystallized fcc Ru catalysts with maximum exposure of [111] facets should be the key design principle to achieve optimum HOR activity since the [111] facets displayed relatively inertness to adsorption of oxygen and moderate adsorption energy of hydrogen in DFT calculation predictions, which endow the remarkable HOR activity of the fcc Pt@Ru tetrahedron/C catalyst. Qiu et al reported an up to 20-fold HOR activity improvement in both mass and specific activities in a body-centered cubic (bcc) phase PdCu alloy nanoparticles compared with the fcc PdCu counterparts (Figure 6H, I). The bcc phase PdCu alloy was obtained via a wet-chemistry method at a critical temperature above 300°C to achieve the fcc to bcc phase conversion. DFT computations unveil that the conversion to bcc phase strengthens the OH binding while keeping a similar H binding strength with that of fcc counterpart, and both of the OH and H binding strengths are comparable to those of Pt surfaces (Figure 6G). The contribution of bcc phase formation is thereby determined to be enhancing the oxophilicity of the surface, which accounts for the improved activity for HOR in alkaline conditions. The above studies both displayed the capability of phase modulation in modifying catalytic activity of the noble metal nanocrystals for HOR reaction. The essential highlight of these two studies is that the phase modulation adjusts the binding of oxygen species independently, without affecting the hydrogen binding strength. This individual modulation of adsorbate binding strength is of
profound significance in the development of catalysts with optimum activity, since the separate modulation of adsorbate binding strengths is frequently restricted by the scaling relationship. Therefore, phase-modulated noble metal nanocrystals have a huge potential in HOR catalysis.

### 4.3 Oxygen reduction reaction

Oxygen reduction reaction is the cathode reaction of the fuel cell. It has been extensively studied for decades since it has complex reaction pathways and mechanisms, and the sluggish reaction rate limits the performance of fuel cell, which is a promising clean energy device for sustainable development in the future. Noble metals have been recognized as the most efficient ORR catalyst candidates, especially Pt which possesses the best ORR catalytic activity among pure metals. However, the scarcity and high cost of noble metals, also the yet to be improved efficiency of pure noble metal catalysts, severely limit the large-scale practical application of fuel cell systems. Thus, material scientists are endeavoring to design and synthesize highly efficient noble metal catalysts while cutting the usage of noble metals by means of alloying, fine control of the shapes, sizes, and morphologies of the noble metal nanocrystals. As the role of the crystal phase in determining the catalytic properties is getting recognized, crystal phase modulation has become another promising technique for the preparation of optimal ORR catalysts. Moreover, since the strain is commonly found in the modulated crystal phases or an important driving force of phase transformation, the crystal phase modulation may contribute to the enhancement of catalytic activity with a combination of the strain effect, which has been under heated discussion in regard to its ability in tuning the surface reactivity of catalysts. This concept has been confirmed in reported cases that fct phase demonstrates better ORR activity than fcc phase in noble metal nanocrystals. For instance, Zhang et al reported the fct phase displayed superior ORR activity to that of fcc phase, in the study of a core-shell FePt/Pt nanoparticles (Figure 7A-C). The mechanism behind is exactly the Pt surface strain modulation by the fct phase as suggested by the quantum mechanics-molecular mechanics simulations. They further optimized the Pt strain effect by partial substitution of Fe by Cu, which resulted in the optimal ORR activity of FeCuPt/Pt nanoparticles. A DFT calculation work of a Pt-based L10 face-centered tetragonal core in core/shell structure nanoparticle also reveals that the improved ORR activity is originated from the unique shear strain in the tetragonal core but not the cubic one. Besides, previous works have also demonstrated the better durability of fct phase. Therefore, obtaining the unconventional fct phase in noble metal nanocatalysts should be a promising direction in ORR catalyst development. Following this concept, in recent times, a new type of face-centered tetragonal (fct) PdFe-alloy nanoparticle-encapsulated Pd (fct-PdFe@Pd) anchored onto nitrogen-doped graphene (NG) hybrid was developed by Maiti et al. An synergistic effect of the PdFe-core and Pd-shell structure was observed, which induced a compressive lattice strain modifying the electronic band structure of Pd-shell by means of incorporation of Fe. The overbinding of oxygenated species which is present in fcc-PdFe nanoparticles is thus sufficiently weakened to moderate strength which enhances the ORR activity.

![FIGURE 6](image-url)
There is also a strong spin-orbit coupling along the crystallographic c direction, which stabilizes the fct-PdFe@Pd structure and enhances the durability.40 Besides the fct phase, phases with hexagonal symmetry also have strain different from the conventional cubic symmetry phases. An investigation of the ORR activity of Pd5Ce and Pt5Ce also addressed the issue of the effect of the crystal phase to ORR activity of noble metal catalysts.90 The surface of Pd5Ce would be under tensile strain when the phase is in cubic symmetry (L-Pd5Ce phase) and compressive strain when the phase is in hexagonal symmetry (H-Pd5Ce phase). As a result, the L-Pd5Ce phase that is under tensile strain displayed less ORR activity in electrochemical tests, which is consistent with DFT results.

In conclusion, the ORR activity of noble metal nanocatalysts can be improved by the formation of novel phases other than the conventional fcc phase, for instance, the fct phase and hexagonal symmetry phase in Pd5Ce. Such phases may display different lattice strains, which account for the catalytic activity adjustment by phase modulations. Meanwhile, structures that have tetragonal symmetry could be conveniently produced with the methods introduced above, such as the epitaxial growth or via the internal strain of the fivefold twinning structures. It could be expected that more ORR efficient noble metal catalysts can be synthesized via strain-induced phase transformation.

4.4 | Oxygen evolution reaction

Oxygen evolution reaction has attracted much attention since it has an essential role in energy conversion and storage. Specifically, it is indispensable for applications such as fuel cells, rechargeable metal-air batteries, and water splitting reaction for hydrogen production.91 Therefore, similarly, development of OER catalysts with high efficiency and low expenses are in huge demand. Noble metals are again the mostly studied candidates for the OER owing to their great intrinsic reactivity toward OER, especially Ru- and Ir-based catalysts.3 However, without the delicate design of the nanoparticle catalyst, noble metal nanoparticles may suffer from loss of reactivity and low durability in long runs of OER, especially for Ru and Pt. The Ir nanoparticles are identified as the desirable OER catalyst since they exhibit remarkable catalytic activity as well as durability.3 Besides the common techniques in nanoengineering, crystal phase engineering is considered to be another efficient means to optimize the catalytic activity and extend the durability.92,93

FIGURE 7  A and B, ORR performance of Pt, fct-FePt/Pt, fcc-FeCuPt/Pt, and fct-FeCuPt/Pt NPs. C, ORR durability test of fct-FeCuPt/Pt NPs.9 Reprinted with permission. Copyright 2014 American Chemical Society. D-F, ORR activity comparison between fct-PdFe@Pd@NG and NG, Fe/NG, Pd/NG, and fcc-PdFe/NG.40 Reprinted with permission. Copyright 2018 American Chemical Society. ORR, oxygen reduction reaction.
The crystal phase modulation for noble metal OER nanocatalysts is still at the primitive stage. Yet, Fan et al have reported the synthesis of 4H/fcc-Au@M (M = Ir, Os, IrOs) core-shell nanoribbons for OER electrocatalysis. The direct growth of Ir on 4H/fcc-Au nanoribbons resulted in a fcc-Ir shell, and this strategy was further applied to the synthesis of 4H/fcc-Au@Os and 4H/fcc-Au@IrOs core-shell nanoribbons. In the generated Au@Os and Au@IrOs core-shell structures, the Au core remained 4H/fcc phase while the Os and IrOs shell crystallized into hcp phase, which is considered as the effect of the lattice mismatch strain between the 4H/fcc-Au nanoribbon surface and the Os and IrOs growing layer. The electrochemical measurement revealed an about fourfold improvement in mass activity compared to the commercial Ir/C catalyst (Figure 8).41 The excellent OER activity could be attributed to the synergistic effect of Au-Ir core-shell, the dendritic surface morphology with abundant atomic kinks and steps, and the uncommon crystal structure of 4H/fcc-Au@fcc-Ir nanoribbons.

The application of crystal phase modulation in OER is less investigated compared to other aforementioned reactions. Nevertheless, the great potential of crystal phase modulation in activating noble metal nanocrystal toward catalysis of various reaction guarantees should not be overlooked in the development of noble metal catalysts toward OER. Moreover, it would be of profound significance if the less-preferred noble metal elements for OER, for instance, Pt, Pd, and Ru can be activated by the crystal phase modulation.

5 | CONCLUSION AND PERSPECTIVES

For a long period, the crystal phase modulation of noble metal nanoparticles has been out of the central research focus of nanoengineering, possibly because of the well-known fact that noble metals have a thermodynamically strong preference to crystallize into the closest-packed structures. Nonetheless, since the prominent influence of
the crystal phase on the crystal properties has been recognized, there is an increasing research interest in crystal phase modulation. Among the many commonly available methods for crystal phase modulation, the strain is frequently presented in the mechanism of the procedures or preserved in the final crystal phase-modified products. In the synthesis of crystal phase-modulated nanocrystals, strain generally acts as the driving force of phase transformation by inducing structural deformation (the internal lattice strain in twinning structure) or directing the growing direction of the crystal phase (epitaxial growth). In the meantime, strain also exists in the distorted structures and unconventional phases, for instance, the face-centered tetragonal (fct) phase. It has been widely reported that lattice strain can adjust the surface adsorption strength and thereby modulate the catalytic activity of the material. Thus, the catalytic activity of strain-induced phase-modulated materials can also be optimized by the strain present in the structure, which broadens the possible design pathways for highly efficient noble metal nanocatalysts. Although the development of crystal phase modulation and investigation of phase-dependent crystal properties are still in a primitive stage, the promising potential of this technique has attracted growing research interest. Besides developing catalysts with crystal phase modulation techniques, recently the novel hydrogen storage Pd nanomaterial was identified and the internal lattice strain in the pentagonal cyclic twinned structure was determined to be the origin of its excellent hydrogen storage ability. This successful case of novel hydrogen storage material suggests us the great potential of crystal phase and strain engineering, as well as the enormous possibilities opened by this technique.

The future studies in strain modulation of phase transformation still need to tackle with these major challenges: (a) the novel phases of Pt, Os, Ir have not been discovered except for epitaxial growth of their novel phase on templates; (b) development of general method to achieve phase-controlled synthesis of noble metal nanomaterials. So far, the epitaxial growth with selective removal of a novel phase template (eg, 4H-Au nanoribbon) is considered as the potential general strategy. (c) The currently widely used wet-chemical methods are unable to obtain high purity of novel crystal phase nanomaterials. Further study of properties and application of novel crystal phase nanomaterials thus requires a synthesis strategy to achieve high purity in both crystal phase and morphology. (d) Theoretical simulation and calculation should be applied to gain deeper insight into the phase transformation mechanism and provide guidance for experimental work. (e) The relationship and difference between the crystal phase and crystal facets remain an open question. (f) Although the internal lattice strain in the novel phase has been proven to be capable of tuning the catalytic activity, a deeper understanding of how to adjust the magnitude of strain at will is needed to achieve optimal activity and for practical applications. It is expected that once these challenges are solved, fruitful advances in the understanding of crystal phase and strain engineering on noble metal will be obtained.

CONFLICT OF INTEREST
The authors declare no conflict of interest.

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