Highly Surface-Distorted Pt Superstructures for Multifunctional Electrocatalysis

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performance eminancement remains chanenging. Herein, we report a new class of Pt superstructures (SSs) with surface distortion engineering by electrochemical leaching of PtTe_x SSs that can largely boost the oxygen reduction reaction (ORR), the methanol oxidation reaction (MOR), and the hydrogen evolution reaction (HER). In particular, the high-distortion (H)-Pt SSs achieve a mass activity of 2.24 A mg⁻¹ at 0.90 V_{RHE} for the ORR and 2.89 A mg⁻¹ for the MOR as well as a low overpotential of 25.3 mV at 10 mA cm⁻² for the HER. Moreover, the distorted surface features of Pt SSs can be preserved by mitigating the detrimental effects of agglomeration/degradation during long-time electrocatalysis. A



multiscale modeling demonstrates that surface compressions, defects, and nanopores act in synergy for the enhanced ORR performance. This work highlights the advances of stable superstructure and distortion engineering for realizing high-performance Pt nanostructures.

KEYWORDS: nanosheet, superstructure, platinum, surface distortion, electrocatalysis

P latinum (Pt), a Holy Grail element in various catalysts, is highly efficient in catalyzing many energy conversion and storage processes with high energy barriers and sluggish kinetics, including for the oxygen reduction reaction (ORR), the methanol oxidation reaction (MOR), and the hydrogen evolution reaction (HER).^{1–5} Up to now, although tremendous efforts have been devoted to designing Pt catalysts due to their inherent advantages over other metals,^{6–11} its large-scale commercial applications are still largely prohibited due to the particularly high cost of Pt.^{12–16} Therefore, the development of new strategies for creating desirable structures of Pt catalysts is highly significant, particularly for the simultaneous realization of superior activity and stability, but is still formidably challenging.

In addition to many conventional strategies (e.g., alloying Pt with earth-abundant transition metals, shaping Pt-based nanostructures, and constructing Pt-based hybrid nanomaterials) for improving the performance of Pt-based nano-catalysts,^{10,11,17–20} creating distorted nanostructures has emerged as a promising approach for the enhanced performance of Pt-based nanocatalysts, because the distinct catalytic sites originating from the atomic rearrangement usually feature unique reactivity.^{9,21–23} The generally adopted approaches for creating a highly distorted structure preferably employ Pt-based alloys with a high surface atomic ratio via electrochemi-

cally or chemically etching away the transition metals, which favors a surface atomic rearrangement to generate more distorted active sites.^{21,23} However, it is still a great challenge to prevent the distorted structure from coarsening and agglomerating under harsh conditions.²⁴ Therefore, developing a Pt catalyst with a highly distorted surface structure at the atomic level and strong macrostructure stability simultaneously is highly desirable.

The layered assembly superstructures (SSs) are privileged in terms of surface atomic ratio and structural stability,^{25–28} which are extremely beneficial for creating active and stable distorted structures. In this study, we created a class of Pt SSs with a controlled distortion structure through electrochemical leaching of PtTe_x SSs. Detailed characterizations demonstrate that the modulation of the distortion degree of Pt SSs is enabled by electrochemical leaching of PtTe_{1.0} SSs, PtTe_{1.5} SSs, and PtTe_{1.0} SSs with controlled compositions and phases, producing high-distortion (H)-Pt SSs, medium-distortion (M)-

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Figure 1. Morphological and structural characterizations of $PtTe_{2.0}$ SSs. (a) HAADF-STEM image. (b, c) High-magnification TEM images. (d) XRD pattern of $PtTe_{2.0}$ SSs. (e) A series of reconstructed 3D tomograms at different viewing angles and their section. (f) HAADF-STEM-EDS elemental mappings and (g) line-scan analysis of $PtTe_{2.0}$ SSs.

Pt SSs, and low-distortion (L)-Pt SSs, respectively. Among these catalysts, the H-Pt SSs exhibit the best activity toward the ORR/MOR/HER with a mass activity of 2.24 A mg⁻¹ for the ORR, 2.89 A mg⁻¹ for the MOR, and a low overpotential of 25.3 mV at 10 mA cm⁻² for the HER. Moreover, the H-Pt SSs, M-Pt SSs, and L-Pt SSs display greatly enhanced stability in comparison with the commercial Pt/C. A multiscale modeling with combined molecular dynamics (MD) and density functional theory (DFT) calculations further testified to the key role of the surface compressions, surface defects, and nanopores on the porous Pt nanosheets that function together in the enhanced ORR performance of distorted Pt SSs. This study provides a new strategy for creating high-performance Pt nanostructures with controlled distortion structures for potential applications.

The pristine $PtTe_{2.0}$ SSs were synthesized through a facile solvothermal approach by using $Pt(acac)_2$ and $Te(OH)_6$ as precursors with the combined use of CO and DL-benzoin (details are given in the Supporting Information). The HAADF-STEM image shows that the $PtTe_{2.0}$ SSs are highly dispersed with a uniform size distribution (the average diameter and length are ~84 ± 8 and ~780 ± 40 nm, respectively) (Figure 1a and Figure S1a-c). The layered assembly is clearly demonstrated by the enlarged TEM images (Figure 1b,c). The Pt/Te composition is determined to be around 1/2 by the SEM-EDS and ICP-OES results (Figure S1d). The XRD peaks can be attributed to the trigonal phase of $PtTe_2$ ($P\overline{3}m1$ (No. 164), JCPDS No. 18-0977) (Figure 1d).^{29,30} To obtain more detailed structure information on $PtTe_2$ SSs, a 3D tomographic reconstruction from the 2D TEM images was carried out (Figure 1e and video S1). The reconstructed 3D visualization of an individual $PtTe_2$ SS at different angles clearly demonstrates the layered assembly structure and obvious tubular feature from a thin slice section. The homogeneous distribution of Pt and Te in $PtTe_2$ SSs is further confirmed by the HAADF-STEM-EDS elemental mappings and line-scan analysis (Figure 1f,g). The lower peak intensities of Pt and Te in the central area of the line scans also indicate the tubular structure of $PtTe_2$ SSs.

PtTe_x SSs with different compositions can be readily synthesized by simply controlling the amount of the Te precursor while other conditions are kept the same (details are given in the Supporting Information). As shown in Figures S2 and S3, there are no distinct morphological differences among these PtTe_x SSs. The corresponding composition variations in PtTe_{1.0} and PtTe_{1.5} SSs were verified by SEM-EDS and ICP-OES results. The elemental distributions of Pt and Te in $PtTe_{1.0}$ and $PtTe_{1.5}$ are also uniform throughout the entire SSs. Furthermore, the thickness characteristics of these $PtTe_x$ SSs were studied by HRTEM images and a corresponding equalized rainbow color mode. The chromatic images display the regular thickness distributions in accordance with the layered assembly structure of PtTe_x SSs (Figure S4). Notably, PtTe₂ is the dominant phase in these PtTe₂ SSs, while the Pt phase can also be detected in both PtTe_{1.0} and PtTe_{1.5} SSs (Figure S5a,d,g). The above results demonstrate the successful preparation of different PtTe_x SSs with controlled compositions and phases.

Letter



Figure 2. Morphological and structural characterizations of different distorted Pt SSs/C. (a–c) Structure models (left) and HAADF-STEM images (right) and (d–f) the equalized rainbow color modes from the corresponding HRTEM images in Figure S10 of (a, d) H-Pt SSs/C, (b, e) M-Pt SSs/C, and (c, f) L-Pt SSs/C. The equalized rainbow colors ranging from red (high) to purple (low) obviously display the thickness differences of these samples. (g) Comparison between the measured planar spacing (d_m) and the original standard planar spacing (d_o) through the statistical HRTEM results in Figure S10.

The generation of distorted Pt SSs/C is readily realized through electrochemical leaching of Te.^{31,32} The CV behavior of these PtTe_x SSs in 0.1 M HClO₄ was acquired, after PtTe_x SSs were loaded on carbon powder to prepare the $PtTe_x SSs/C$ (Figure S6). During the activation process of $PtTe_x$ SSs, a dramatic CV profile evolution occurs, where the continuous decrease of oxidation peak intensity of Te and the augmentation of underpotentially deposited hydrogens of Pt_{Hud} were clearly observed, indicating the massive leaching of Te and enrichment of Pt of the catalysts (Figure S5b,e,h). In view of various surface atomic rearrangements caused by different Te contents, the resulting distorted Pt SSs from PtTe_{2.0} SSs, PtTe_{1.5} SSs, and PtTe_{1.0} SSs are denoted as the H-Pt SSs/C, M-Pt SSs/C, and L-Pt SSs/C, respectively. It is noted that the CV profiles become stable after 500 cycles, where the maximum electrochemical surface area (ECSA) is obtained. The gradient increase of ECSA demonstrates the massive Te leaching and greater exposure of Pt active sites in these Pt SSs/C. The electrochemical leaching brings about an evident phase transformation, where only Pt diffraction peaks are observed for H-Pt SSs/C, M-Pt SSs/C, and L-Pt SSs/C (Figure S5c,f,i). The SEM-EDS and ICP-OES results also

reveal that the Te content in H-/M-/W-Pt SSs is negligible (Figure S7).

Among these distorted Pt SSs/C, the tubular superstructure is largely maintained, while obvious distorted and porous features among the assembly layers are observed (Figure 2a-c and Figure S8). The HAADF-STEM images coupled with EDS elemental mappings and line-scan analysis also reveal the removal of most of the Te in PtTe, SSs after the electrochemical process (Figure S9). To reveal the distorted structure generated by electrochemical Te dissolution, the thickness distribution of these catalysts was also studied by HRTEM images and the corresponding equalized rainbow color modes. The chromatic images display a conspicuous thickness difference with random and distorted distributions among these Pt SSs/C (Figure 2d-f), representing the dramatic morphology variability caused by atomic rearrangement. Furthermore, a comparison between the measured planar spacing (d_m) and the original standard planar spacing (d_{o}) through statistical HRTEM results was carried out to display the d_m fluctuation ranges caused by the distorted structure (Figure S10). As observed in Figure 2g, dramatic deviations were observed for the H-Pt SSs/C, which is clearly pubs.acs.org/NanoLett



Figure 3. ORR performance and characterizations after durability tests. (a) ORR polarization curves, (b) bar graph of the mass activity and specific activity, and (c) evolution of mass activities and specific activities after different potential cycles of the H-Pt SSs/C, M-Pt SSs/C, L-Pt SSs/C, and commercial Pt/C. (d, e) TEM images, (f) HRTEM image (the areas outlined by white dotted lines represent the pore structures), and (g) a comparison between the measured planar spacing (d_m) and original standard planar spacing (d_o) through statistical HRTEM results of the H-Pt SSs/C after ORR durability tests.

distinguishable from those of M-Pt SSs/C and L-Pt SSs/C, suggesting that the highest distortion degree is established in the H-Pt SSs/C. The above results demonstrate that the engineering of distortion degree was successfully achieved by using the composition- and phase-controlled $PtTe_x$ SSs as the starting materials.

To shed light on the effect of distortion on performance, the catalytic properties of these Pt SSs/C toward the ORR were initially measured in acid electrolyte and benchmarked against the commercial Pt/C (Figure S11). Figure 3a shows the ORR polarization curves of the H-Pt SSs/C, M-Pt SSs/C, L-Pt SSs/ C, and commercial Pt/C. Obviously, the half-wave potential and onset potential of the H-Pt SSs/C is shifted considerably to the highest potential in comparison to those of the M-Pt SSs/C, L-Pt SSs/C, and commercial Pt/C, indicating that the H-Pt SSs/C has the highest ORR activity among these catalysts. The kinetic currents at 0.90 V_{RHE} from the ORR polarization curves were also normalized to the Pt mass loadings and surface areas to generate mass and specific activities, respectively (Figure 3b). We can see that the H-Pt SSs/C exhibits the highest mass activity of 2.24 A mg_{Pt}^{-1} , which is 1.2, 2.9, and 8.9 times higher than the mass activities of the M-Pt SSs/C (1.92 A mg_{Pt}^{-1}), L-Pt SSs/C (0.77 A mg_{Pt}^{-1}), and commercial Pt/C (0.25 A mg_{Pt}^{-1}), respectively. Moreover, the H-Pt SSs/C exhibits a specific activity as high as 4.52 mA cm^{-2} , more than 1 order of magnitude higher than that for the commercial Pt/C (0.39 mA cm⁻²). Figure 3c charts the evolution of the mass and specific activities of these Pt SSs/C and commercial Pt/C during the durability test process, which was performed at a potential between 0.6 and 1.1 V_{RHE} at a sweep rate of 100 mV s⁻¹ (Figure S12). It reveals that there was only 10.3% mass activity and 3.6% specific activity loss for the H-Pt SSs/C, while the commercial Pt/C shows a much larger decrease in mass activity (47.4%). The H-Pt SSs/C after the ORR durability tests was characterized further. The overall structure of the H-Pt SSs/C is largely preserved after ORR durability tests, and a tubular layered assembly structure also can be observed (Figure 3d,e). The maintenance of porous and distorted features was further identified by HRTEM results (Figure 3f and Figure S13). Moreover, the statistical HRTEM results demonstrate a slight variation of the $d_{\rm m}$ fluctuation range in the H-Pt SSs/C after the durability tests (Figure 3g). In sharp contrast, the commercial Pt/C displays an obvious size change and serious aggregation after the durability test (Figure S14). These results collectively confirm that the SSs are highly stable during the long-term electrocatalysis and the distorted surface features can

Letter



Figure 4. Computational simulations. (a) Atomic structure after 2000 ps of a classical MD simulation for a 50 × 50 nm porous Pt nanosheet. (b) Radial distribution functions of the porous Pt nanosheet at 300 K (red) and of the perfect Pt bulk crystal (gray). (c) Enlarged view of a nondefective and strained area in the nanosheet (left) and the corresponding color-coded strain distribution in the area (right). (d) Enlarged view of a one-atomic-layer-deep nanopit in the nanosheet. (e) ΔE_O value of the pure Pt (111), the defect-free Pt nanosheet with -3% compression, the Pt nanosheet with a one-atomic-layer-deep nanopit, and the Pt nanosheet with a nanopore. The optimal E_O is set to 0. The corresponding atomic models are shown in insets: navy and red spheres represent Pt and O atoms, respectively.

be preserved by efficiently mitigating the detrimental effects of agglomeration and degradation.

MD and DFT calculations were further carried out to elucidate the origin of the enhanced catalytic activity and stability of Pt SSs. To characterize the typical surface distortion in Pt SSs on an atomic scale, we constructed a 50×50 nm Pt nanosheet of three-atomic-layer thickness (~110000 atoms) comprising multiple nanopores and surface edges (Figure 4a). We first performed classical MD simulations at 300 K to examine the atomic structure of the nanosheet on the basis of the embedded-atom method.³³ We find that the porous nanosheet can maintain its mechanical integrity and thermodynamic stability at 300 K, as evidenced by welldefined peaks of the radial distribution function (RDF) in Figure 4b, which corroborates the HAADF-STEM observation on the stability of SSs (Figure 2). More importantly, all RDF peaks of the porous nanosheet shift downward in comparison to those of the perfect Pt lattice, suggesting that surface compressions develop in the porous Pt nanosheet with shortened Pt-Pt distances. The MD simulations revealed that compressive strains of up to -5% developed in the nondefective surface region (Figure 4c) with an average compression of about -3%. In addition, nanoscale thinning adjacent to the nanopores is also observed in the nanosheet, as illustrated in Figure 4d.

We subsequently carried out DFT calculations to examine how the presence of the surface compressions, the surface thinning, and the nanopores would affect the ORR activity. To this end, four atomic models were constructed to calculate the oxygen binding energy ($E_{\rm O}$) on the Pt surfaces, with the results being shown in Figure 4e. These models include the perfect Pt

(111) surface, a defect-free Pt nanosheet with -3%compression, a Pt nanosheet with a shallow pit (one-atomiclayer deep), and a Pt nanosheet with a nanopore. E_0 has been widely used as a descriptor for ORR activity on metal surfaces, and there is an optimal E_0 value at which the ORR activity reaches its maximum.³⁴ Here, for convenience, we shifted the optimal E_0 to zero and used ΔE_0 to represent the difference of a given E_0 value relative to this optimal reference. Although Pt (111) is an excellent ORR catalyst, it binds oxygen too strongly $(\Delta E_0 = -0.2 \text{ eV})$, which suppresses its ORR activity. Interestingly, this overbinding problem is mitigated on the compressive Pt nanosheet, the Pt nanosheet with a shallow pit, and the nanosheet with a nanopore, with the corresponding $\Delta E_{\rm O}$ values being calculated as 0.082, 0.076, and -0.048 eV, respectively. Allof these values are much closer to the optimal value in comparison to thatof the perfect Pt (111) surface (-0.2 eV). Thus, the surface compressions, the surface defects, and the nanopores all contribute to enhanced ORR activity on the porous Pt nanosheet, which explains the experimental observations that the distorted Pt SSs exhibit much higher mass and specific activities in comparison to the commercial Pt/C. Furthermore, the fact that the H-Pt SSs possess a more flexible and fluffy aggregation of nanosheets and higher densities of nanopores in nanosheets (Figure S8) among these three superstructures suggests that the H-Pt SSs are highly efficient electrocatalysts for the ORR.

The catalytic properties of these Pt SSs/C toward the MOR and HER were also investigated. Figure S15a shows the electrooxidation curves of different catalysts in 0.1 M HClO₄ containing 0.5 M CH₃OH. The H-Pt SSs/C, M-Pt SSs/C, and L-Pt SSs/C exhibit mass activities of 2.89, 1.86, and 0.87 A

mg⁻¹, respectively, 5.7, 3.6, and 1.7 times higher than that of the commercial Pt/C (0.51 A mg⁻¹). The specific activities of the above catalysts also show a similar trend (Figure S15b). Figure S15c shows the enhanced MOR durability of these distorted Pt SSs/C, where the current density of these distorted Pt SSs/C decreased slowly but the commercial Pt/ C showed a rapid initial decay with only 16% of the initial current density being retained. For HER performance, the LSV curves (with Ohmic drop correction) at a scan rate of 5 mV s^{-1} in 1.0 M KOH were investigated for these catalysts (Figure S15d). The Pt loading was fixed at 0.01 mg cm⁻². The H-Pt SSs/C exhibits the smallest overpotential at a current density of 10 mA cm⁻² (25.3 mV), Tafel slope (24.8 mV decade⁻¹), and charge transfer resistance (24.6 Ω) in comparison to the M-Pt SSs/C (34.3 mV, 34.2 mV decade⁻¹, 26.5 Ω), L-Pt SSs/ C (59.4 mV, 56.5 mV decade⁻¹, 32.3 Ω), and the commercial Pt/C (39.8 mV, 47.3 mV decade⁻¹, 30.2 Ω), suggesting the fastest HER kinetics at the interface of H-Pt SSs/C and the electrolyte (Figures S15e and S16). The durability of H-Pt SSs/C was then evaluated by chronopotentiometry at a constant current density of 10 mA cm⁻² in 1.0 M KOH electrolyte (Figure S15f), where these distorted Pt SSs/C exhibits negligible degradation after 10 h, while the commercial Pt/C shows rapid decay in the beginning.

In summary, we have successfully created a series of unique Pt SSs/C with a controlled distortion structure for the ORR/ MOR/HER. Taking advantage of easy Te leaching for the $PtTe_x$ SSs with controlled compositions and phases, we readily realized the distortion modulation through electrochemical leaching. Due to the highly distorted structure and abundant active sites, the H-Pt SSs/C exhibits superior ORR/MOR/ HER activities relative to those of M-Pt SSs/C, L-Pt SSs/C, and commercial Pt/C. Significantly, these distorted Pt SSs/C generally display excellent electrocatalytic stability in comparison with commercial Pt/C, because the distorted surface features in SSs can be largely preserved by efficiently mitigating the detrimental effect of agglomeration and degradation. The MD and DFT calculations demonstrated that the surface compressions, surface defects, and nanopores cause synergistic effects on the enhanced ORR performance of these distorted Pt SSs. This work highlights the importance of the combined structure and distortion engineering for developing highly active and stable Pt catalysts for catalysis and beyond.

ASSOCIATED CONTENT

1 Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.nanolett.1c00902.

Chemicals, experimental and characterization details, electrochemical measurements, DFT calculations, TEM images, SEM-EDS and ICP-OES results, HRTEM images, HAADF-STEM images, line scans, and corresponding elemental mappings of PtTe_{2.0} SSs, PtTe_{1.5} SSs and PtTe_{1.0} SSs, TEM images and successive CV curves of different PtTe_x SSs/C, TEM images, XRD patterns, SEM-EDS, and ICP-OES results, HRTEM images, HAADF-STEM images, line scans, and corresponding elemental mappings of H-Pt SSs/C, M-Pt SSs/C, and L-Pt SSs/C, TEM images, CV curves, and polarization curves of commercial Pt/C, HRTEM image of H-Pt SSs/C after the ORR durability test, CV curves, polarization curves, chronopotentiometry curves, Tafel

plots, and EIS spectra of H-Pt SSs/C, M-Pt SSs/C, L-Pt SSs/C, and commercial Pt/C (PDF)

3D tomographic reconstruction for PtTe₂ SSs (MPG)

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Author Contributions

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Author Contributions

X.H. conceived and supervised the research. X.H., L.B., and Y.F. designed the experiments. X.H., L.B., Y.F., and Q.S. performed most of the experiments and data analyses. Z.Z. and

G.L. performed the MD and DFT calculations. X.H., L.B., Y.F., Q.S., L.L., F.L., J.W., and X.Z. participated in various aspects of the experiments and discussions. X.H., Y.F., Z.Z., G.L., and Q.S. wrote the paper. All authors discussed the results and commented on the manuscript.

Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Shao, M.; Chang, Q.; Dodelet, J.; Chenitz, R. Recent advances in electrocatalysts for oxygen reduction reaction. *Chem. Rev.* **2016**, *116*, 3594–3657.

(2) Zhu, C.; Du, D.; Eychmüller, A.; Lin, Y. Engineering ordered and nonordered porous noble metal nanostructures: synthesis, assembly, and their applications in electrochemistry. *Chem. Rev.* **2015**, *115*, 8896–8943.

(3) Sheng, W.; Myint, M.; Chen, J.; Yan, Y. Correlating the hydrogen evolution reaction activity in alkaline electrolytes with the hydrogen binding energy on monometallic surfaces. *Energy Environ. Sci.* **2013**, *6*, 1509–1512.

(4) Li, L.; Wang, P.; Shao, Q.; Huang, X. Metallic nanostructures with low dimensionality for electrochemical water splitting. *Chem. Soc. Rev.* **2020**, *49*, 3072–3106.

(5) Bianchini, C.; Shen, P. K. Palladium-based electrocatalysts for alcohol oxidation in half cells and in direct alcohol fuel cells. *Chem. Rev.* **2009**, *109*, 4183–4206.

(6) Chang, J. F.; Feng, L. G.; Liu, C. P.; Xing, W.; Hu, X. L. Ni_2P enhances the activity and durability of the Pt anode catalyst in direct methanol fuel cells. *Energy Environ. Sci.* **2014**, *7*, 1628–1632.

(7) Wang, Y.; Zhao, N.; Fang, B.; Li, H.; Bi, X. T.; Wang, H. Carbon-supported Pt-based alloy electrocatalysts for the oxygen reduction reaction in polymer electrolyte membrane fuel cells: particle size, shape, and composition manipulation and their impact to activity. *Chem. Rev.* **2015**, *115*, 3433–3467.

(8) Huang, H.; Li, K.; Chen, Z.; Luo, L.; Gu, Y.; Zhang, D.; Ma, C.; Si, R.; Yang, J.; Peng, Z.; Zeng, J. Achieving remarkable activity and durability toward oxygen reduction reaction based on ultrathin Rh-doped Pt nanowires. *J. Am. Chem. Soc.* **2017**, *139*, 8152–8159.

(9) Chattot, R.; Bacq, O. L.; Beermann, V.; Kühl, S.; Herranz, J.; Henning, S.; Kühn, L.; Asset, T.; Guétaz, L.; Renou, G.; Drnec, J.; Bordet, P.; Pasturel, A.; Eychmüller, A.; Schmidt, T. J.; Strasser, P.; Dubau, L.; Maillard, F. Surface distortion as a unifying concept and descriptor in oxygen reduction reaction electrocatalysis. *Nat. Mater.* **2018**, *17*, 827–833.

(10) Zhao, Z.; Liu, H.; Gao, W.; Xue, W.; Liu, Z.; Huang, J.; Pan, X.; Huang, Y. Surface-engineered PtNi-O nanostructure with record-high performance for electrocatalytic hydrogen evolution reaction. *J. Am. Chem. Soc.* **2018**, *140*, 9046–9050. (11) Wang, P.; Jiang, K.; Wang, G.; Yao, J.; Huang, X. Phase and interface engineering of platinum-nickel nanowires for efficient electrochemical hydrogen evolution. *Angew. Chem., Int. Ed.* **2016**, *55*, 12859–12863.

(12) Chu, S.; Cui, Y.; Liu, N. The path towards sustainable energy. *Nat. Mater.* **2017**, *16*, 16–22.

(13) Wang, S.; Jiang, S. P. Prospects of fuel cell technologies. *Natl. Sci. Rev.* 2017, 4, 163–166.

(14) Cano, Z. P.; Banham, D.; Ye, S.; Hintennach, A.; Lu, J.; Fowler, M.; Chen, Z. Batteries and fuel cells for emerging electric vehicle markets. *Nat. Energy* **2018**, *3*, 279–289.

(15) Norskov, J. K.; Christensen, C. H. Toward efficient hydrogen production at surfaces. *Science* **2006**, *312*, 1322–1323.

(16) Morales-Guio, C. G.; Stern, L. A.; Hu, X. Nanostructured hydrotreating catalysts for electrochemical hydrogen evolution. *Chem. Soc. Rev.* **2014**, *43*, 6555–6569.

(17) Tiwari, J. N.; Sultan, S.; Myung, C. W.; Yoon, T.; Li, N.; Ha, M.; Harzandi, A. M.; Park, H. J.; Kim, D. Y.; Chandrasekaran, S. S.; Lee, W. G.; Vij, V.; Kang, H.; Shin, T. J.; Shin, H. S.; Lee, G.; Lee, Z.; Kim, K. S. Multicomponent electrocatalyst with ultralow Pt loading and high hydrogen evolution activity. *Nat. Energy* **2018**, *3*, 773–782. (18) Yin, H.; Zhao, S.; Zhao, K.; Muqsit, A.; Tang, H.; Chang, L.; Chang, T. J.

Zhao, H.; Gao, Y.; Tang, Z. Ultrathin platinum nanowires grown on single-layered nickel hydroxide with high hydrogen evolution activity. *Nat. Commun.* **2015**, *6*, 6430.

(19) Cao, Z.; Chen, Q.; Zhang, J.; Li, H.; Jiang, Y.; Shen, S.; Fu, G.; Lu, B.; Xie, Z.; Zheng, L. Platinum-nickel alloy excavated nanomultipods with hexagonal close-packed structure and superior activity towards hydrogen evolution reaction. *Nat. Commun.* **2017**, *8*, 15131. (20) Wang, L.; Zhu, Y.; Zeng, Z.; Lin, C.; Giroux, M.; Jiang, L.; Han, Y.; Greeley, J.; Wang, C.; Jin, J. Platinum-nickel hydroxide nanocomposites for electrocatalytic reduction of water. *Nano Energy* **2017**, *31*, 456–461.

(21) Chen, S.; Niu, Z.; Xie, C.; Gao, M.; Lai, M.; Li, M.; Yang, P. Effects of catalyst processing on the activity and stability of Pt-Ni nanoframe electrocatalysts. *ACS Nano* **2018**, *12*, 8697–8705.

(22) Li, M.; Zhao, Z.; Cheng, T.; Fortunelli, A.; Chen, C.; Yu, R.; Zhang, Q.; Gu, L.; Merinov, B. V.; Lin, Z.; Zhu, E.; Yu, T.; Jia, Q.; Guo, J.; Zhang, L.; Goddard, W. A.; Huang, Y.; Duan, X. Ultrafine jagged platinum nanowires enable ultrahigh mass activity for the oxygen reduction reaction. *Science* **2016**, *354*, 1414–1419.

(23) Strasser, P.; Koh, S.; Anniyev, T.; Greeley, J.; More, K.; Yu, C.; Liu, Z.; Kaya, S.; Nordlund, D.; Ogasawara, H.; Toney, M. F.; Nilsson, A. Lattice-strain control of the activity in dealloyed core-shell fuel cell catalysts. *Nat. Chem.* **2010**, *2*, 454–460.

(24) Cui, C.; Gan, L.; Heggen, M.; Rudi, S.; Strasser, P. Compositional segregation in shaped Pt alloy nanoparticles and their structural behaviour during electrocatalysis. *Nat. Mater.* **2013**, *12*, 765–771.

(25) Jiang, H.; Ren, D.; Wang, H.; Hu, Y.; Guo, S.; Yuan, H.; Hu, P.; Zhang, L.; Li, C. 2D Monolayer MoS₂-carbon interoverlapped superstructure: engineering ideal atomic interface for lithium ion storage. *Adv. Mater.* **2015**, *27*, 3687–3695.

(26) Shi, Z.; Kang, W.; Xu, J.; Sun, Y.; Jiang, M.; Ng, T.; Xue, H.; Yu, D. Y. W.; Zhang, W.; Lee, C. Hierarchical nanotubes assembled from MoS₂-carbon monolayer sandwiched superstructure nanosheets for high-performance sodium ion batteries. *Nano Energy* **2016**, *22*, 27–47.

(27) Tan, C.; Luo, Z.; Chaturvedi, A.; Cai, Y.; Du, Y.; Gong, Y.; Huang, Y.; Lai, Z.; Zhang, X.; Zheng, L.; Qi, X.; Goh, M. H.; Wang, J.; Han, S.; Wu, X.; Gu, L.; Kloc, C.; Zhang, H. Preparation of highpercentage 1T-phase transition metal dichalcogenide nanodots for electrochemical hydrogen evolution. *Adv. Mater.* **2018**, *30*, 1705509.

(28) Lu, Q.; Yu, Y.; Ma, Q.; Chen, B.; Zhang, H. 2D transitionmetal-dichalcogenide-nanosheet-based composites for photocatalytic and electrocatalytic hydrogen evolution reactions. *Adv. Mater.* **2016**, *28*, 1917–1933.

(29) Yan, M.; Huang, H.; Zhang, K.; Wang, E.; Yao, W.; Deng, K.; Wan, G.; Zhang, H.; Arita, M.; Yang, H.; Sun, Z.; Yao, H.; Wu, Y.; Fan, S.; Duan, W.; Zhou, S. Lorentz-violating type-II Dirac fermions in transition metal dichalcogenide PtTe₂. *Nat. Commun.* **2017**, *8*, 257.

(30) Ma, H.; Chen, P.; Li, B.; Li, J.; AI, R.; Zhang, Z.; Sun, G.; Yao, K.; Lin, Z.; Zhao, B.; Wu, R.; Tang, X.; Duan, X. Thickness-tunable synthesis of ultrathin type-II Dirac semimetal $PtTe_2$ single crystals and their thickness-dependent electronic properties. *Nano Lett.* **2018**, *18*, 3523–3529.

(31) Feng, Y.; Huang, B.; Yang, C.; Shao, Q.; Huang, X. Platinum porous nanosheets with high Surface distortion and Pt utilization for enhanced oxygen reduction catalysis. *Adv. Funct. Mater.* **2019**, *29*, 1904429.

(32) Li, H.; Zhao, S.; Gong, M.; Cui, C.; He, D.; Liang, H.; Wu, L.; Yu, S. Ultrathin PtPdTe nanowires as superior catalysts for methanol electrooxidation. *Angew. Chem., Int. Ed.* **2013**, *52*, 7472–7476.

(33) Zhou, X. W.; Johnson, R. A.; Wadley, H. N. G. Misfit-energyincreasing dislocations in vapor-deposited CoFe/NiFe multilayers. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2004**, *69*, 144113–144123.

(34) Nørskov, J. K.; Rossmeisl, J.; Logadottir, A.; Lindqvist, L.; et al. Origin of the overpotential for oxygen reduction at a fuel-cell cathode. *J. Phys. Chem. B* **2004**, *108*, 17886–17892.