# In Situ Formed Pt<sub>3</sub>Ti Nanoparticles on a Two-Dimensional Transition Metal Carbide (MXene) Used as Efficient Catalysts for Hydrogen **Evolution Reactions**

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Supporting Information

ABSTRACT: The design of efficient catalysts capable of delivering high currents at low overpotentials for hydrogen evolution reactions (HERs) is urgently needed to use catalysts in practical applications. Herein, we report platinum (Pt) alloyed with titanium (Ti) from the surface of  $Ti_3C_2T_3$ MXenes to form Pt<sub>3</sub>Ti intermetallic compound (IMC) nanoparticles (NPs) via in situ coreduction. In situ X-ray absorption spectroscopy (XAS) indicates that Pt undergoes a temperature-dependent transformation from single atoms to intermetallic compounds, and the catalyst reduced at 550 °C exhibits a superior HER performance in acidic media. The Pt/



 $Ti_3C_2T_4$ -550 catalyst outperforms commercial Pt/Vulcan and has a small overpotential of 32.7 mV at 10 mA cm<sup>-2</sup> and a low Tafel slope of 32.3 mV dec<sup>-1</sup>. The HER current was normalized by the mass and dispersion of Pt, and the mass activity and specific activity of Pt/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>-550 are 4.4 and 13 times higher, respectively, than those of Pt/Vulcan at an overpotential of 70 mV. The density functional theory (DFT) calculations suggest that the (111)- and (100)-terminated  $Pt_3Ti$  nanoparticles exhibit \*H binding comparable to Pt(111), while the (110) termination has an \*H adsorption that is too exergonic, thus poisoned in the low overpotential region. This work demonstrates the potential of MXenes as platforms for the design of electrocatalysts and may spur future research for other MXene-supported metal catalysts that can be used for a wide range of electrocatalytic reactions.

**KEYWORDS:** Intermetallic compounds, MXenes, in situ reduction, hydrogen evolution reaction

ydrogen evolution reactions (HERs) are a critical link between renewable energy sources and energy conversion applications such as hydrogen fuel cells.<sup>1</sup> At present, the most efficient elemental metal electrocatalyst in acidic media is platinum (Pt).<sup>2,3</sup> However, Pt is scarce and expensive, necessitating the development of catalysts with a reduced precious metal content and enhanced activity.<sup>4</sup> To fulfill the cost-effective utilization of Pt, the number of active sites has been increased, for example, by reducing the particle size, and the activity of each active site has been boosted via tuning the local electronic structure.<sup>5,6</sup> Alloying Pt with nonnoble metals represents an effective route for simultaneously reducing the Pt amount and enhancing the intrinsic activity of electrocatalysts.<sup>7,8</sup> Moreover, Pt-alloyed nanoparticles (NPs) can be prepared with various compositions and tunable structures, and their thermodynamic stability benefits catalyst regeneration in industrial applications.<sup>10</sup> As a result, Pt-based alloy NPs with controlled particle sizes are an attractive alternative strategy for promoting HER activity.<sup>11</sup> Well-dispersed bimetallic NPs have altered electronic structures with optimized binding to the reaction intermediate \*H, and their use is promising to realize the two main strategies<sup>4</sup> (i.e., increasing the number of active sites and enhancing the reactivity of each active site) employed for designing HER catalysts.

Platinum-based intermetallic compounds (IMCs) represent an important class of materials in electrocatalysis due to their well-defined structural and tunable electronic properties.<sup>12</sup>

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**Figure 1.** Aberration-corrected HAADF-STEM. (a) HAADF-STEM image of  $Pt_3Ti$  NPs on a  $Ti_3C_2T_x$  MXene support reduced at 550 °C. (b, c) EDS analysis of the  $Pt_3Ti$  NPs. (d, e) Atomic resolution HAADF-STEM image of  $Pt/Ti_3C_2T_x$ -550. Insets of d and e show the FFT pattern of a NP and sphere models of the  $Pt_3Ti$  (110) surface, respectively. (f) Simulated STEM image of  $Pt_3Ti$  along the [110] direction; inset shows the face centered cubic (fcc) structure of the  $Pt_3Ti$  IMC.

Among IMCs, Pt alloyed with early transition metals is wellknown for its superior thermal and chemical stabilities owing to the presence of strong Lewis acid and base interactions.<sup>1</sup> For instance, Pt<sub>3</sub>Ti has one of the largest formation enthalpies (-298 kJ/mol) found among Pt-based IMCs.<sup>14</sup> However, early transition metals (denoted as M) are more oxyphilic compared to late transition metals and main group metals,<sup>15</sup> and thus, the standard reduction potentials of platinum and M salts are quite different (e.g., the standard reduction potentials of Ti<sup>2+</sup> and  $[PtCl_4]^{2-}$  are -1.63 V and +0.73 V, respectively), leading to barriers in their coreduction at a similar rate to form intermetallic NPs.<sup>16</sup> To reduce and incorporate M metals into the Pt lattice of a particle with a controlled size, strong reducing agents (e.g., potassium triethylborohydride) and organic capping ligands, such as oleylamine, are often employed, but these reagents require complicated experimental procedures and may form carbonaceous species that block the active sites.<sup>17</sup> Therefore, the synthesis of Pt-M IMCs through chemical coreduction remains a significant challenge, and a facile method to obtain Pt-M IMCs will benefit their study and application.

Recently, the family of two-dimensional (2D) early transition metal carbides (MXenes), especially  $Ti_3C_2T_x$  (where T represents surface terminations such as -O and -OH), has garnered attention for electrocatalysis due to its high electronic conductivity and hydrophilic nature.<sup>18</sup> However, the electrocatalytic performance of these materials is impaired by the limited number of active sites on the surface of the carbides.<sup>19</sup> Therefore, MXene-based hybrid structures are often desired to enhance the electrochemical activity.<sup>20–22</sup> Herein, we report the in situ formation of Pt<sub>3</sub>Ti intermetallic nanoparticles (iNPs) on 2D titanium carbide ( $Ti_3C_2T_x$ ) as an efficient electrocatalyst for HERs. The extent of IMC

formation and the size of iNPs depend on the annealing temperature, and 550 °C is the optimal reduction temperature for achieving the highest HER activity, due to the enhanced electrical conductivity and optimized \*H adsorption strength of the catalyst. The catalyst demonstrates a superior HER performance, as it has a lower overpotential, smaller Tafel slope, greater stability, higher mass, and better specific activity compared to commercial platinum/Vulcan (Pt/C) catalysts.

In general, the bulk Ti<sub>3</sub>AlC<sub>2</sub> synthesized via spark plasma sintering was etched by HF to obtain the 2D Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> MXene (Figure S1a).<sup>23</sup> A series of characterizations were conducted to confirm the two-dimensionality of the MXene support. The powder X-ray diffraction (XRD) pattern (Figure S1b) shows that the most intense peaks corresponding to the nonbasal plane of Ti<sub>3</sub>AlC<sub>2</sub> ( $2\theta \approx 39^{\circ}$ ) disappear after the HF treatment, and the (002) peak of the  $Ti_3C_2T_x$  MXene shifts to a lower angle, indicating that the lattice parameter has expanded along the [001] direction. The SEM image (Figure S1c) illustrates the exfoliation along the basal plane, where  $Ti_3C_2T_x$  exhibits an accordion-like morphology that is typical of the MXene family.<sup>18</sup> After sonication (see the Supporting Information),  $Ti_3C_2T_r$  nanosheets with curved edges can be obtained (Figure S2a), and the selected area electron diffraction (SAED) pattern indicates the hexagonal symmetry inherited from bulk Ti<sub>3</sub>AlC<sub>2</sub> (inset of Figure S2b). Atomic force microscopy (AFM) was employed to study the thickness of the  $Ti_3C_2T_x$  nanosheets (Figure S3). The AFM height profile, denoted by the solid line, shows that the  $Ti_3C_2T_x$  flake has different thicknesses; the thinner part is approximately 4.5 nm thick (trilayer),<sup>24</sup> and the height of the thicker part is 18 nm, which corresponds to multilayers of  $Ti_3C_2T_x$ .

Platinum precursors were then loaded onto the resulting  $Ti_3C_2T_x$  MXene (denoted as  $Pt/Ti_3C_2T_x$ ) by incipient wetness



**Figure 2.** In situ X-ray absorption spectroscopy. (a) The Pt  $L_{III}$  edge in situ XANES spectra of the Pt/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> catalyst reduced at different temperatures compared to that of Pt/SiO<sub>2</sub>. (b) The magnitude of the Fourier transform of the  $k^2$  weighted Pt  $L_{III}$  edge in situ EXAFS of Pt/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> reduced at different temperatures compared to that of Pt/SiO<sub>2</sub>.

impregnation (IWI), which was followed by a subsequent reduction under a H<sub>2</sub> atmosphere at 550 °C (see the Supporting Information for detailed procedures). High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) shows that the NPs are well-distributed on the MXene support with an average diameter of  $6.6 \pm 3.5$  nm (Figure 1a and Figure S5). To study the composition of the NPs, an energy-dispersive X-ray spectroscopy (EDS) line scan was performed on an NP hanging over the vacuum (to avoid signals from the support). The spectra (Figure 1b,c) show that the Ti and Pt signals are evenly distributed throughout the NP; core-shell structures were not observed, and neither element segregated on the surface. The atomic resolution HAADF-STEM image (Figure 1d) shows the ordered intermetallic structures of a NP. The superlattice spots in the fast Fourier transform (FFT) pattern (Figure 1d, inset) further confirm the formation of the Pt<sub>3</sub>Ti IMC phase. The interplanar spacings measured for the {110} and {001} planes are 2.78 and 3.91 Å, respectively, which matches the expected interplanar spacings of a Cu<sub>2</sub>Au-type Pt<sub>3</sub>Ti IMC. A NP was viewed along the [110] zone axis (Figure 1e); two alternating columns were observed, where the brighter columns consist of all Pt atoms, and the darker columns alternate between Pt (green spheres) and Ti atoms (pink spheres). The experimental STEM image agrees well with the simulated image obtained for L<sub>12</sub> ordered Pt<sub>3</sub>Ti nanoalloys (Figure 1f), indicating that Pt<sub>3</sub>Ti is formed by the in situ coreduction of the Pt precursor and  $Ti_3C_2T_x$  MXene.

To investigate the influence of the reduction temperature on the chemical environment of the formed IMCs, in situ X-ray absorption spectroscopy (XAS) was conducted. Fresh Pt/  $Ti_3C_2T_x$  samples were reduced at four different temperatures (200, 400, 550, and 700  $^{\circ}$ C, designated as Pt/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>-200, Pt/ Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>-400, Pt/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>-550, and Pt/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>-700, respectively), and a Pt/SiO<sub>2</sub> sample reduced at 550 °C was used as the reference. The particle sizes of the catalysts were first studied by STEM, and the Pt/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>-400, Pt/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>-550, and  $Pt/Ti_3C_2T_x$ -700 samples were shown to have particle sizes of  $5.3 \pm 2.1$ ,  $6.6 \pm 3.5$ , and  $9.0 \pm 4.1$  nm, respectively (Figures S4–S6). In contrast, bright spots are observed in the STEM image of Pt/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>-200, implying that single Pt atoms formed on the MXene support (Figure S7). In the in situ X-ray absorption near edge structure (XANES) spectra obtained at the Pt L<sub>III</sub> edge (Figure 2a), Pt/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>-200 has a much higher intensity than the other  $Pt/Ti_3C_2T_x$  catalysts, indicating that the Pt precursor is not reduced at 200 °C.<sup>25</sup> The white lines in the XANES spectra obtained for the  $Pt/Ti_3C_2T_x$ catalysts reduced at other temperatures are slightly narrower

and more intense compared to that of Pt/SiO<sub>2</sub>, indicating a change in the energy of the unoccupied *d* states for samples reduced at different temperatures.<sup>26</sup> The XANES energies of Pt/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>-200, Pt/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>-550, and Pt/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>-700 (11.5653, 11.5646, and 11.5648 keV) are higher than that of Pt/SiO<sub>2</sub> (11.5640 keV), while the energy of Pt/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>-400 (11.5640 keV) is identical to that of Pt/SiO<sub>2</sub>. The disparity in the XANES energies indicates that the density of the unoccupied 5d states of Pt is altered by reducing Pt/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> at various temperatures.

The magnitude of the Fourier transform of the extended Xray absorption fine structure (EXAFS) spectra (Figure 2b) shows that the  $Pt/Ti_3C_2T_x$  catalysts reduced at 400, 550, and 700 °C have a central peak with a higher intensity than that of Pt/SiO<sub>2</sub> due to the in-phase constructive interference between the scattering of Pt-Pt and Pt-Ti. In contrast, the results of EXAFS show that the Pt-Pt contribution at approximately 2.5 Å is absent in  $Pt/Ti_3C_2T_r$ -200, indicating the presence of atomic Pt species. Fitting the EXAFS spectra (Figure S8) reveals the coordination numbers (CNs) and bond distances of Pt, as summarized in Table S1. The fitting results of Pt/  $Ti_3C_2T_x$ -200 show 4.1 Pt-N(O) bonds at 2.06 Å, suggesting that the Pt precursor is not fully reduced at 200 °C, and Pt remains as single atoms on the MXene support. This result is consistent with the STEM results. The EXAFS spectrum of Pt/  $Ti_3C_2T_r$ -400 is slightly different from that of the monometallic Pt supported on SiO<sub>2</sub>; the fit gives 8.5 Pt–Pt bonds at 2.75 Å and, potentially, a very minor contribution from a second scattering path (0.3 Pt-Ti bonds at 2.74 Å), implying the formation of Pt NPs and a small amount of surface Pt-Ti alloy. Increasing the reduction temperature to 550 °C leads to the fitting results showing 6.6 Pt-Pt bonds at 2.75 Å and 3.4 Pt-Ti bonds at 2.75 Å. The ratio of Pt-Pt CN to Pt-Ti is ~2, which is consistent with that of the ideal Pt<sub>3</sub>Ti structure, which features 8 Pt-Pt bonds and 4 Pt-Ti bonds for each Pt atom (where the total CN of  $Pt/Ti_3C_2T_x$ -550 is less than 12 due to the unsaturated bonds on the NP surfaces). The formation of Pt<sub>3</sub>Ti IMC nanoparticles in Pt/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>-700 is also confirmed by atomic resolution HAADF-STEM (Figure S9). Annealing the sample at 700 °C results in larger CNs and, likely, further Ti enrichment in the NPs. The Pt-Pt and Pt-Ti CNs increase to 7.2 and 4.1, respectively, with minor changes in the bond distances (Table S1). Notably, the total CN increases with increasing annealing temperatures, indicating an increase in the average particle size, which is consistent with the results of STEM. The XRD patterns (Figure S10) show that the shoulder peak at  $\sim 40^{\circ}$  can be attributed to the (111) planes



**Figure 3.** Electrochemical characterizations. (a) HER polarization curves at 2 mV s<sup>-1</sup> in H<sub>2</sub> saturated 0.1 M HClO<sub>4</sub> and (b) a magnification of the 0–10 mA region. (c) Mass activity of the Pt/Vulcan and Pt/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> catalysts with different treatments and (d) specific activity of the Pt/Vulcan and Pt/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> catalysts, which is normalized by H<sub>2</sub> chemisorption at -60 °C. (e) Tafel curves calculated by  $\eta = b \log |i| + a$ ; (f) Nyquist plots of Pt/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> reduced at different temperatures and measured at 0 V vs RHE.

of the supported metal in Pt/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> catalysts as it is absent in the XRD pattern obtained for the reduced Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> sample. The shoulder peaks observed in the Pt/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>-550 and Pt/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>-700 XRD patterns deviate from the position of the Pt (111) planes and shift to higher values, implying the formation of IMCs. However, it is challenging to determine the position of the shoulder peaks, as they interfere with peaks of the MXene support, making in situ XAS essential for studying the structures of the supported metal on Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> MXene.

Our results suggest that Pt undergoes a three-stage transformation on the surface of the  $Ti_3C_2T_r$  MXene upon reduction at different temperatures. The temperature-dependent transformation of Pt also sheds light on the mechanism of the formation of Pt<sub>3</sub>Ti. First, unlike conventional supports, such as  $SiO_2$  and  $Al_2O_3$ , where Pt nanoparticles are formed by reducing an impregnated  $Pt(NH_3)_4(NO_3)_2$  precursor with  $H_2$ at 200 °C,<sup>27,28</sup> Pt remains as single atoms on the  $Ti_3C_2T_x$ MXene under the same treatment, implying that the precursor binds strongly on the surface of the MXene. Second, after increasing the reduction temperature to 400 °C, Pt is reduced, as shown by the attenuated intensity in the XANES spectra (Figure 2a). The white line of  $Pt/Ti_3C_2T_x$ -400 is still slightly higher than that of Pt/SiO<sub>2</sub>, while the edge energies are the same, implying the formation of Pt nanoparticles with minor amounts of Pt-Ti alloy present on the NP surfaces. Third, Pt<sub>3</sub>Ti IMCs are formed when the reduction temperature reaches 550 °C, and intermetallic nanoparticles with larger particle sizes are retained at a higher temperature (700 °C). The formation of the IMCs can be attributed to chemical reactions between platinum and the  $Ti_3C_2T_x$  MXene support, which result in the incorporation of Ti into the Pt nanoparticles. The chemical reactions leading to the formation of IMCs in supported metal catalysts are often designated as reactive metal support interactions (RMSIs).<sup>29</sup>

To evaluate the HER performance of the  $Pt/Ti_3C_2T_x$  catalysts, a three-electrode system was used with a H-cell

composed of two counterparts. The Pt counter electrode was separated in one counterpart to avoid Pt contamination, and all of the potentials were automatically IR corrected by the potentiostat. The metal loading (Pt) of the tested catalysts was confirmed by inductively coupled plasma mass spectrometry (ICP-MS), and a similar amount of Pt was used in each electrochemical measurement (Table S2). The different temperatures used to reduce the catalysts led to quite different electrocatalytic activities. As shown in Figure 3a,b, all of the  $Pt/Ti_3C_2T_x$  catalysts have HER activities that are higher than the bare  $Ti_3C_2T_x$  support, which has a large overpotential (576.8 mV) at 10 mA ( $\eta$ @10 mA). Note that the electrical double layer current of the  $Ti_3C_2T_x$  support contributes to the negative current of the  $Pt/Ti_3C_2T_x$  catalysts at zero potential, which is also observed in other MXene-based electrocatalysts.<sup>25</sup> Pt/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>-550 has the smallest overpotential  $\eta$ at both 10 mA (32.7 mV) and 40 mA (60.8 mV), followed by  $Pt/Ti_3C_2T_r$  reduced at 400, 700, and 200 °C (Table S2). Remarkably, the  $\eta @10$  mA of Pt/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>-550 is 23 mV lower than that of a commercial Pt/Vulcan catalyst with the same amount of Pt. Moreover, to avoid the effect of the roughness factor (i.e., the ratio of the catalyst surface area to the geometric surface area) and to provide a fair comparison of the HER activity, the mass activity (i.e., the activity normalized by the mass of Pt) and specific activity (i.e., the activity normalized by the Pt dispersion) are used to reflect the intrinsic activity of the catalysts. The mass activity of Pt/  $Ti_3C_2T_x$ -550 at an overpotential of 50 mV is 1.3 mA  $\mu g^{-1}$ which is 3.3 times greater than that of the commercial Pt/ Vulcan catalyst (0.4 mA  $\mu g^{-1}$ ), as shown in Figure 3c. The disparity in the catalytic activity for HERs of the two catalysts increases at the higher overpotential (70 mV), where the mass activity exhibited by Pt/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>-550 (2.65 mA  $\mu$ g<sup>-1</sup>) is 4.4 times higher than that of the Pt/Vulcan catalyst (0.6 mA  $\mu$ g<sup>-1</sup>). To probe the intrinsic HER activity of  $Pt/Ti_3C_2T_{rt}$  H<sub>2</sub> chemisorption (see the Supporting Information for experimental details) at -60 °C was employed to measure the Pt dispersion, as the electrochemical surface area (ECSA) could not be determined from the hydrogenation sorption peaks in the cyclic voltammetry measurements, and H<sub>2</sub> chemisorption at an ambient temperature was also not successful. The Pt dispersions were determined to be 22.2%, 10.6%, 7.6%, and 3.2% for Pt/Vulcan, Pt/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>-400, Pt/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>-550, and Pt/  $Ti_3C_2T_r$ -700, respectively (Table S3). The specific activity of  $Pt/Ti_3C_2T_x$ -550 at an overpotential of 50 mV was 17.2 mA ( $\mu g$ surface Pt)<sup>-1</sup>, which is 10 times greater than that of commercial Pt/Vulcan (Figure 3d). At a higher overpotential (70 mV), Pt/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>-550 delivered an HER current (34.6 mA  $(\mu g \text{ surface } Pt)^{-1})$  that was 13 times larger than that delivered by Pt/Vulcan (2.7 mA ( $\mu$ g surface Pt)<sup>-1</sup>). Moreover, Pt/  $Ti_3C_2T_x$ -550 has the lowest Tafel slope of 32.3 mV dec<sup>-1</sup> in the range of  $\sim 1-10$  mA, which suggests that Pt/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>-550 has the best HER kinetics among all of the tested catalysts (Figure 3e). This much lower Tafel slope indicates a more rapid increase in the HER current achieved at a lower overpotential. Furthermore, we doubled the amount of commercial Pt/Vulcan catalysts used for HERs (i.e., the amount of Pt is twice that in  $Pt/Ti_3C_2T_x$ -550), and a Tafel slope of 32.3 mV dec<sup>-1</sup> was achieved (Figure S11), which is comparable to that of  $Pt/Ti_3C_2T_x$ -550. This observation further demonstrates that the mass activity of Pt/Ti<sub>3</sub>C<sub>2</sub>T<sub>r</sub>-550 is superior to that of commercial Pt/Vulcan, as only half of the amount of platinum is needed to achieve a similar Tafel slope. We also compared the HER activity of our catalyst with the representative noble metal and heterostructure catalysts reported in the literature (Table S4), and  $Pt/Ti_3C_2T_x$ -550 almost exhibited the lowest overpotential and Tafel slope.

To understand the superior performance of  $Pt/Ti_3C_2T_x$ -550, we measured the double layer capacitance and impedance of all the catalysts. The double layer capacitance  $(C_{dl})$  of the bare support reduced at different temperatures was calculated from the CV curves obtained at different scan speeds. Figure S12 shows that C<sub>dl</sub> decreased with increasing reduction temperatures; the  $C_{dl}$  of Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>-400, Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>-550, and Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>-700 were 77.28, 53.41, and 35.38 mF cm<sup>-2</sup>, respectively. Figure S13 shows a further decrease in the  $C_{dl}$  of the Pt/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>-400, Pt/  $Ti_3C_2T_x$ -550, and Pt/ $Ti_3C_2T_x$ -700 catalysts compared to that of their corresponding bare supports, due to the reaction between the MXene support and Pt precursors. The Pt/  $Ti_3C_2T_x$ -400 and Pt/ $Ti_3C_2T_x$ -550 catalysts have similar  $C_{dl}$ values, which are 50% higher than the  $C_{dl}$  of Pt/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>-700; therefore, Pt/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>-700 possesses a lower specific capacitance and hence smaller surface area than those of  $Pt/Ti_3C_2T_r$ -400 and  $Pt/Ti_3C_2T_x$ -550. Lowering the reduction temperature leads to less Ti being incorporated from the surface of the MXene, and increasing the reduction temperature causes the particles to agglomerate, which reduces the number of the active sites for HERs. The Nyquist plot of Pt/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>-550 measured at 0 V shows a much smaller semicircle compared to the Nyquist plots of Pt/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>-400 and Pt/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>-700 (Figure 3f), indicating that  $Pt/Ti_3C_2T_x$ -550 has the lowest charge transfer resistance (among the three catalysts) during the initial HER process. Note that the bare  $Ti_3C_2T_x$  support reduced at 550 °C exhibits a large resistance at 0 V (Figure S14), presumably due to the oxidation of the support after exposing the reduced samples to air, which is consistent with our previous work.<sup>30</sup> This result suggests that the increased charge transfer at the initial state in Pt/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>-550 results from the formation of Pt<sub>3</sub>Ti nanoparticles with controlled

sizes. The formed  $Pt_3Ti$  IMCs modulate the adsorptive properties of the active sites that are well-dispersed on the MXene support, leading to the fast Faradaic process and superior HER kinetics.

We also performed X-ray photoelectron spectroscopy (XPS) to investigate the change in the MXene support upon reduction (Figure S15). High-resolution XPS spectra in the Ti 2p region show that the peaks can be deconvoluted into components corresponding to Ti<sup>4+</sup>, Ti<sup>3+</sup>, Ti<sup>2+</sup>, and Ti-C. The XPS spectra show that the reduction of  $Pt/Ti_3C_2T_r$  leads to the oxidation of the  $Ti_3C_2T_x$  support, which is consistent with the results of XRD and the previous study.<sup>30</sup> The surface ratio of Ti-C/Ti determined by XPS is 54.80%, 16.40%, 27.43%, and 18.61% for Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>, Pt/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>-400, Pt/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>-550, and  $Pt/Ti_3C_2T_x$ -700, respectively. These XPS results indicate that Pt/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> reduced at 550 °C preserves most Ti-C structures, while the extent of the surface oxidation of Pt/  $Ti_3C_2T_x$ -400 and  $Pt/Ti_3C_2T_x$ -700 is higher. The surface oxidation leads to a higher charge transfer resistance, which impairs the HER activity of Pt/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>-400 and Pt/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>-700.

The stability of  $Pt/Ti_3C_2T_x$ -550 was then tested via an accelerating stability test (AST) by sweeping the potential between -0.2 and 0.1 V. The HER activity after 1000 and 2000 cycles of the AST was compared with the original HER polarization curve (Figure 4a). Interestingly, after the 1000th



**Figure 4.** Stability test of the in situ formed  $Pt_3Ti$  nanoparticle catalysts and DFT calculations. (a) HER curves before and after the stability tests and (b) an HAADF-STEM image of the used  $Pt/Ti_3C_2T_x$ -550 catalyst (after 1000 cycles), where the inset shows the FFT pattern of a  $Pt_3Ti$  nanoparticle. (c) DFT-calculated free energy diagrams of the hydrogen evolution at the Pt(111),  $Pt_3Ti(111)$ , Pt(100),  $Pt_3Ti(100)$ , Pt(110), and  $Pt_3Ti(110)$  surfaces. The hydrogen coverage was determined to be when the differential adsorption free energy was closest to zero (the structures in the top view are shown).

cycle, the  $\eta @10$  mA reduced by 2.3 mV, which can be attributed to the structural modification of the catalyst surface. Only an increase of 2.5 mV was observed in the 2000th cycle, indicating the excellent stability of Pt/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>-550. The crystal structure of the used Pt/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>-550 catalyst was also investigated by HAADF-STEM. Figure 4b shows that the

{110} and {100} superlattice spots (marked by red circles) are still present in the FFT pattern (inset of Figure 4b), indicating that the structure of  $Pt_3Ti$  is stable during the HER. It should be noted that no obvious Pt or Ti surface segregation was observed in the spent HER catalyst, as indicated by the atomic resolution image (Figure 4b) and the EDS line scan (Figure S16).

Density functional theory (DFT) calculations were carried out to gain further insights into the excellent electrocatalytic performance of Pt/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>-550 for HERs (Figure 4c). The formation energy of the Pt<sub>3</sub>Ti NPs relative to bulk Pt and Ti, as calculated by DFT, is -0.88 eV, which suggests that Pt<sub>3</sub>Ti is thermodynamically stable (see the Supporting Information for details). According to the Pourbaix diagram, Pt<sub>3</sub>Ti is a stable Pt/Ti alloy phase under acidic conditions and applied reduction potentials (Figure S17). The HER pathway can be represented by a three-state diagram with an initial  $(H^+ + e^-)$ state, an intermediate \*H state, and a final 1/2H<sub>2</sub> product.<sup>31</sup> The differential free energy of hydrogen adsorption ( $\Delta G_{\rm H}^*$ ) is a key descriptor of the HER activity, and the optimum value of  $\Delta G_{\rm H}^{*}$  should be close to zero to compromise for the energy barriers of the adsorption and desorption steps.<sup>25</sup> The steadystate hydrogen coverage of each surface is determined to be when the differential adsorption free energy is closest to zero. The  $\Delta G_{\rm H}^*$  values of Pt<sub>3</sub>Ti(111) and Pt<sub>3</sub>Ti(100) surfaces are -0.01 and -0.05 eV, respectively, which are closer to zero or are comparable to the  $\Delta G_{\rm H}^*$  values of Pt(111) (-0.03 eV) and Pt(100) (-0.19 eV). Besides, the Pt<sub>3</sub>Ti (110) has a too exergonic  $\Delta G_{\rm H}^*$  values (-0.28 eV), similar to that of Pt (110) (-0.24 eV). Thus, the (110)-type sites of Pt and the Pt<sub>3</sub>Ti NPs are poisoned in the low overpotential region. We note that Ptterminations were used at the (100) and (110) surfaces because these surfaces have lower surface free energies in a vacuum than their Ti-terminated counterparts. Our calculations indicate that the adsorption of \*H on the  $Pt_3Ti(111)$ and Pt<sub>3</sub>Ti(100) surfaces is neither too strong nor too weak due to the tailored local electronic properties, which indicates that the HER performance of the  $Pt/Ti_3C_2T_x$ -550 catalyst is superior to that of pure Pt. Additionally, the STEM images (Figure 1a and Figure S18) show that the nanoparticles in Pt/  $Ti_3C_2T_x$ -550 and Pt/ $Ti_3C_2T_x$ -700 tend to form cuboctahedral morphologies that are mainly composed of  $\{111\}$  and  $\{100\}$ facets (Figure S9b), which endow the catalysts with increased HER activities. The preference for cuboctahedral-shaped particles can result from the high-temperature annealing and was also observed for Pt<sub>3</sub>Ni nanoparticles.<sup>32</sup> Considering both the DFT results and electrochemical characterization, the reduction temperature plays a pivotal role in the nature of the active sites, which results in temperature-dependent HER activity. Pt<sub>3</sub>Ti outperforms the Pt nanoparticles and unreduced Pt single atoms for HERs, as indicated by both the experimental results and DFT calculations. We note that, although  $Pt_3Ti$  can be retained in the  $Pt/Ti_3C_2T_x$ -700 catalyst, high-temperature reduction (700 °C) leads to the agglomeration of IMCs and a greater oxidation of the MXene support (compared to  $Pt/Ti_3C_2T_x$ -550). The superior HER activity of  $Pt/Ti_3C_2T_x$ -550 results from the in situ formation of  $Pt_3Ti$ IMCs with optimized surface reactivities, which modulates hydrogen adsorption at the active sites, and the less oxidized MXene supports, which benefit charge transfer during the HER process.

In summary, we reported, for the first time, the synthesis of IMC NP electrocatalysts using  $Ti_3C_2T_x$  MXenes as both the

conductive support and the second metal precursor. The resulting Pt<sub>3</sub>Ti nanoparticles were readily formed at 550 °C, and the ordered Pt<sub>3</sub>Ti structure was confirmed by both atomic resolution HADDF-STEM and EXAFS. Compared to the catalysts prepared at other temperatures (200, 400, and 700  $^{\circ}$ C), Pt/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>-550 had the best catalytic performance for HERs, the smallest overpotential of 32.7 mV (@ 10 mA), a Tafel slope of 32.3 mV dec<sup>-1</sup>, and the lowest charge transfer resistance. Furthermore, the catalyst was stable in an acidic solution, and no significant activity loss or structure change (e.g., surface segregation) was observed after the HER cycles. The DFT calculations suggest that the (111) and (100) surfaces of Pt<sub>3</sub>Ti show comparable \*H binding to Pt(111), while the (110) termination has too exergonic \*H adsorption, thus poisoned in the low overpotential region. We believe that this route used to synthesize Pt<sub>3</sub>Ti/MXene catalysts opens a new avenue for designing a wide variety of MXene-supported metal catalysts for electrocatalytic applications.

## ASSOCIATED CONTENT

## **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.nano-lett.9b01381.

Additional details on the experimental materials and methods; XRD, SEM, and HAADF-STEM results; fittings of EXAFS spectra, characterizing the structures of the catalysts; electrochemical analysis and measurements; tables providing quantitative information on the XAS; summarized HER mass and specific activities; literature summary of HER activity in acidic conditions (PDF)

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Z.L. and Z.Q. contributed equally to this work. Z. L. and Y. W. conceived of the concept and designed the experiments. Z.Q., X.L., and W.H. conducted the electrochemical tests. L.Z. and T.M. performed the microscopy experiments. S.W. and H.X. carried out the DFT calculations. Z.W. and J.T. M. performed the XAS measurements. F.L and M.C helped with the XRD characterizations. Z.L., Z.Q., H.X., W.H., and Y.W. wrote the manuscript. All authors discussed the results and commented on the manuscript.

## Notes

The authors declare no competing financial interest.

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