# Supporting Information

**Achieving highly efficient catalysts for hydrogen evolution reaction by electronic state modification of platinum on versatile $Ti_3C_2T_x$ (MXene)**

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**Supplementary Figures**

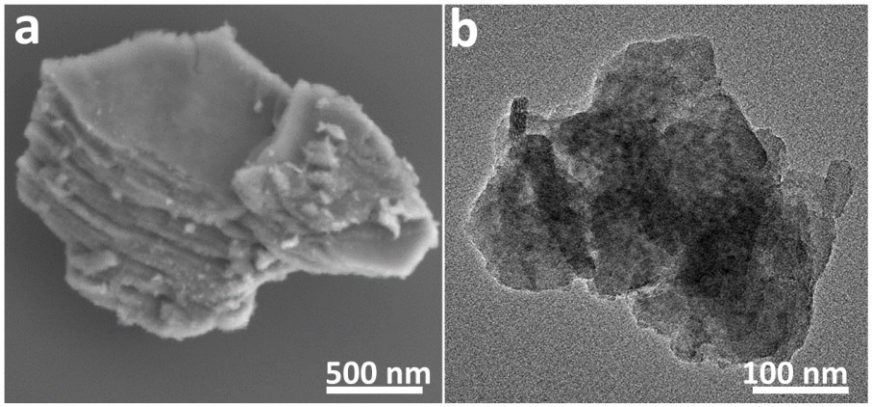



**Figure S1.** Morphological characterization of $Ti_3C_2T_x$. (a) the SEM and (b) TEM characterization of $Ti_3C_2T_x$.

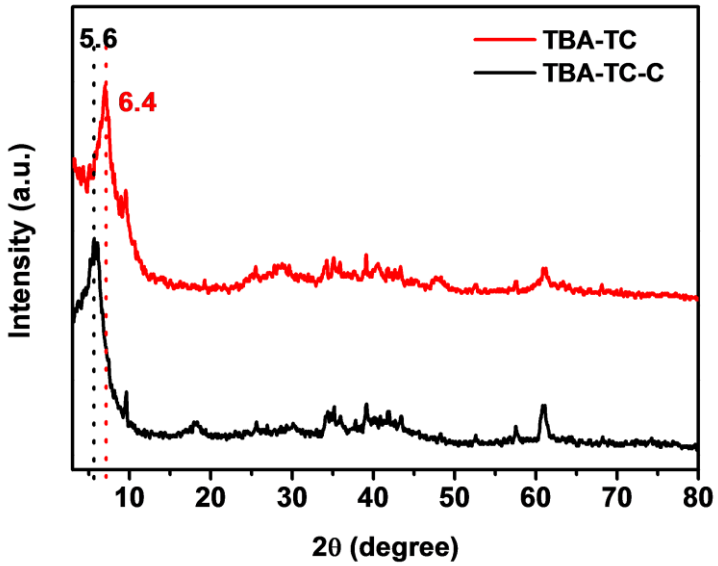



**Figure S2.** XRD patterns of TBA-$Ti_3C_2T_x$ treated with 25 wt% (black) and 2.5 wt% (red) TBAOH solutions.

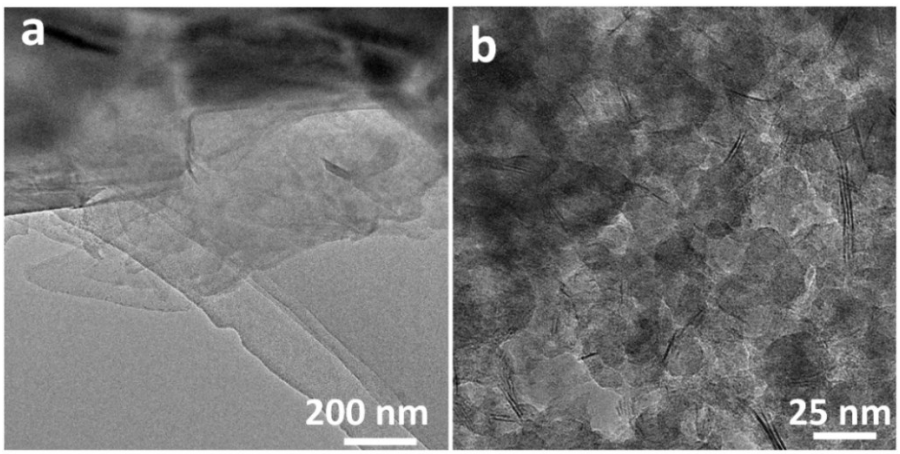


**Figure S3.** TEM characterization of D-$Ti_3C_2T_x$. (a) TEM image of. (b) HRTEM image of D-$Ti_3C_2T_x$ indicating the layers (2-3 layers).

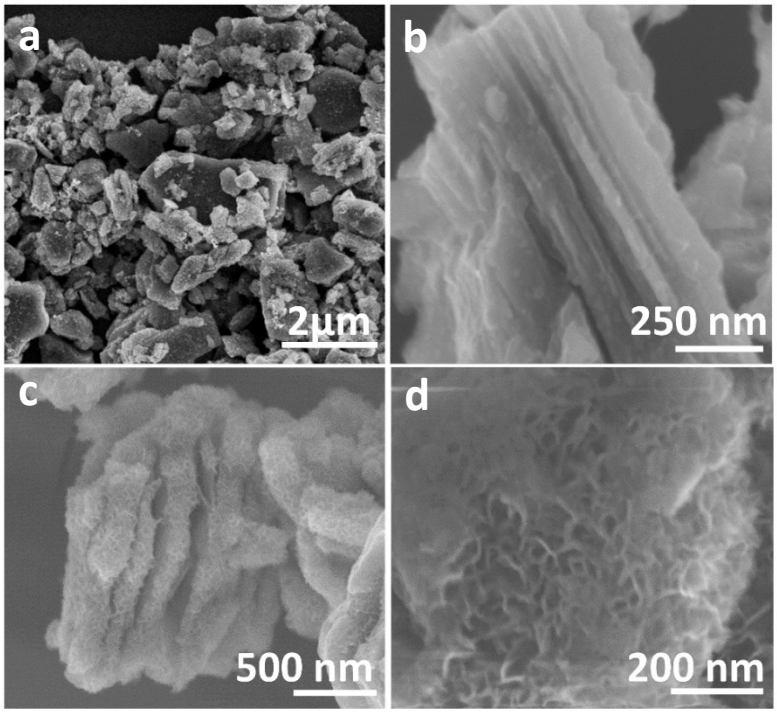



**Figure S4.** Morphological characterization of TBA-$Ti_3C_2T_x$ obtained in different TBAOH concentration. (a) SEM images of TBA-$Ti_3C_2T_x$-c. (b) The enlarged image of (a). (c) SEM images of TBA-$Ti_3C_2T_x$. (d) The enlarged image of (c).

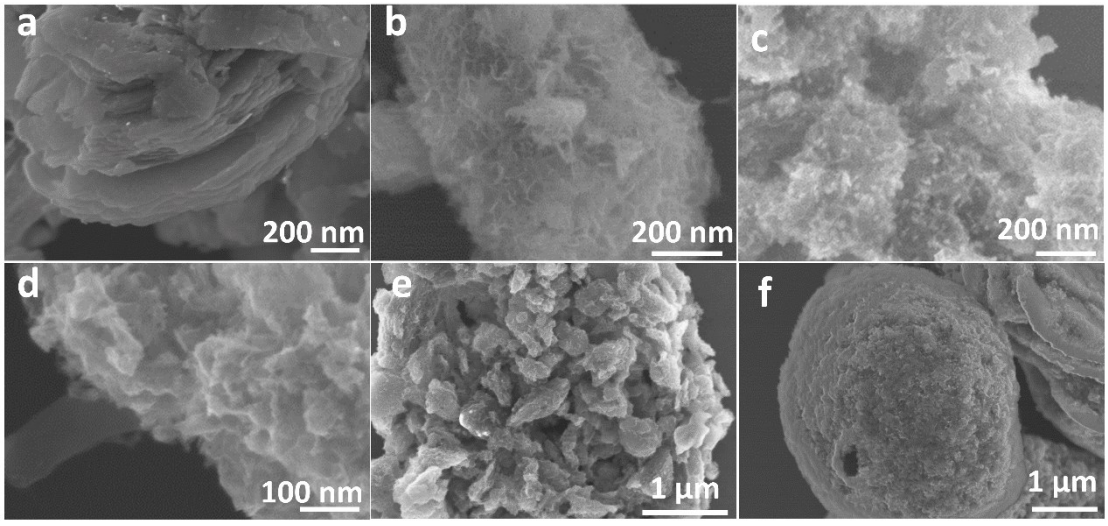



**Figure S5.** Morphological characterization of the supports and the catalysts. (a) SEM images of K-$Ti_3C_2T_x$ (b) SEM image of TBA-$Ti_3C_2T_x$. (c) The morphology of TBA-$Ti_3C_2T_x$-Pt with

the reduction of $NaBH_4$. (d) The morphology of D-$Ti_3C_2T_x$-Pt with the reduction of $NaBH_4$. (e) The morphology of TBA-$Ti_3C_2T_x$-Pt with the method of UV-induced reduction. (f) The morphology of D- $Ti_3C_2T_x$-Pt with the method of UV-induced reduction.

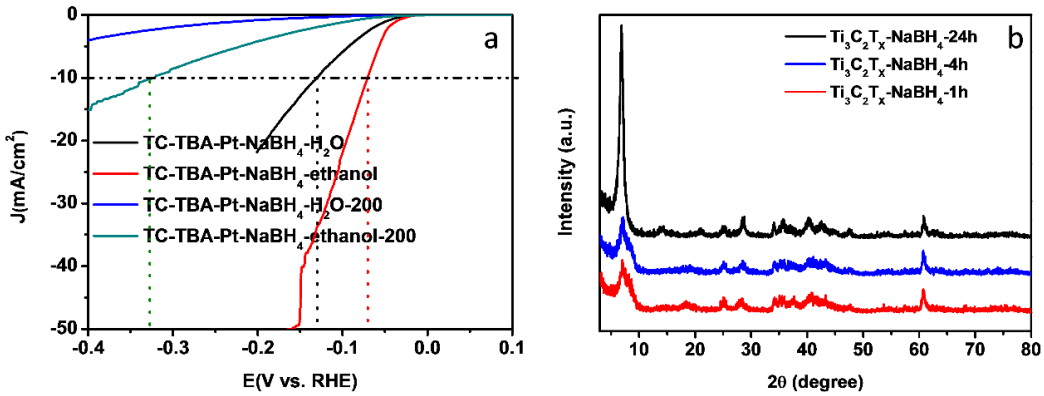



**Figure S6.** Optimization results of the (a) solvent and (b) reaction time in the reduction process by $NaBH_4$.The reduction time and solvent are optimized with a perfect time of 4 h in aqueous solution.

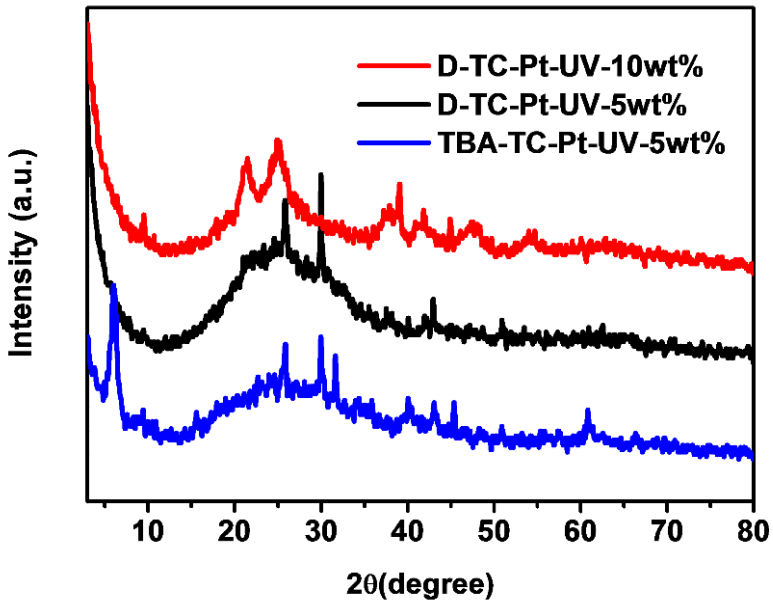
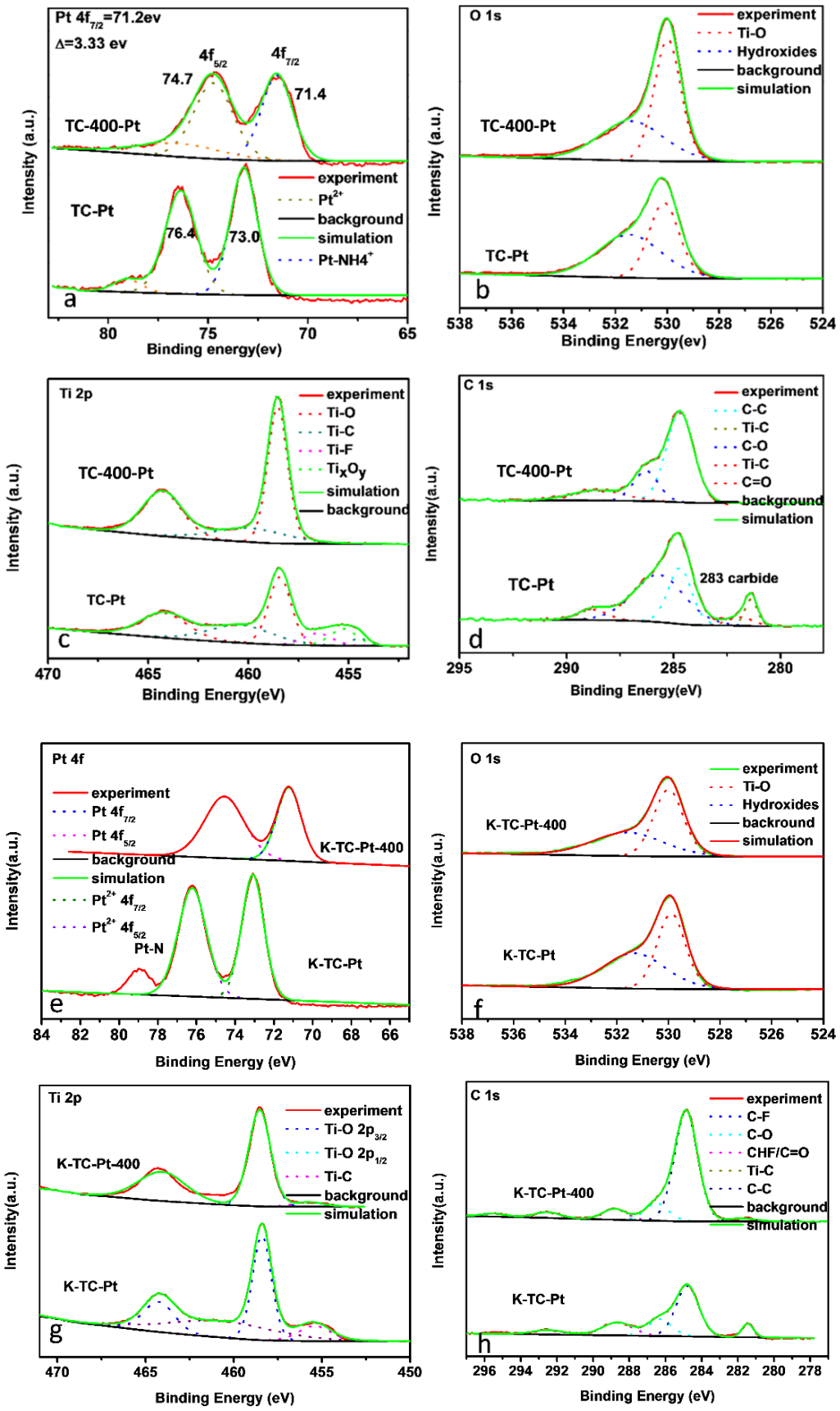



**Figure S7.** XRD patterns of TBA-$Ti_3C_2T_x$-Pt (blue) and D-$Ti_3C_2T_x$-Pt (red and black) obtained by the UV-induced method.


Pt 4f7/2=71.2ev
Δ=3.33 ev
4f5/2
4f7/2
74.7
71.4
TC-400-Pt
TC-Pt
76.4
73.0
experiment
Pt2+
background
simulation
Pt-NH4+
a
Intensity (a.u.)
Binding energy(ev)
O 1s
experiment
Ti-O
Hydroxides
background
simulation
TC-400-Pt
TC-Pt
b
Binding Energy(ev)
Ti 2p
experiment
Ti-O
Ti-C
Ti-F
TixOy
simulation
background
TC-400-Pt
TC-Pt
c
Binding Energy(eV)
C 1s
experiment
C-C
Ti-C
C-O
Ti-C
C=O
background
simulation
TC-400-Pt
TC-Pt
283 carbide
d
Binding Energy(eV)
Pt 4f
experiment
Pt 4f7/2
Pt 4f5/2
background
simulation
Pt2+ 4f7/2
Pt2+ 4f5/2
Pt-N
K-TC-Pt-400
K-TC-Pt
e
Intensity(a.u.)
Binding Energy (eV)
O 1s
experiment
Ti-O
Hydroxides
backround
simulation
K-TC-Pt-400
K-TC-Pt
f
Binding Energy (eV)
Ti 2p
experiment
Ti-O 2p3/2
Ti-O 2p1/2
Ti-C
background
simulation
K-TC-Pt-400
K-TC-Pt
g
Binding Energy (eV)
C 1s
experiment
C-F
C-O
CHF/C=O
Ti-C
C-C
background
simulation
K-TC-Pt-400
K-TC-Pt
h
Binding Energy (eV)

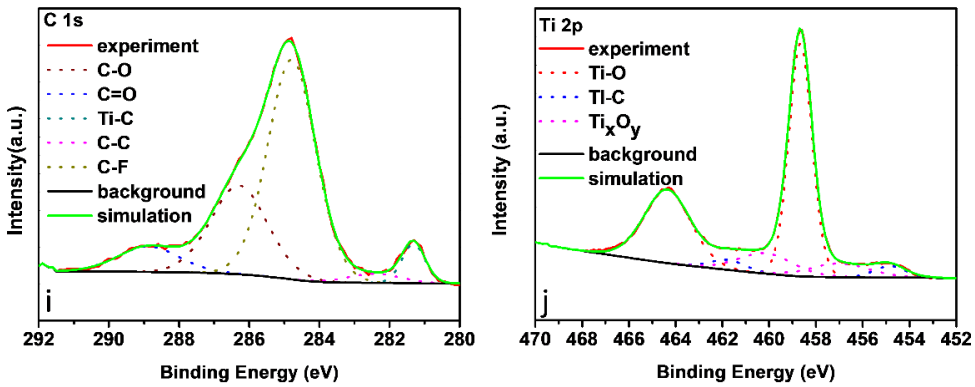



**Figure S8.** XPS results of the catalysts. XPS of the (a) Pt 4f, (b) O 1s, (c) Ti 2p, (d) C 1s spectra of the $Ti_3C_2T_x$-400-Pt-20 and $Ti_3C_2T_x$-Pt-20. XPS results of (e) Pt 4f, (f) O 1s, (g) Ti 2p, (h) C 1s of K-$Ti_3C_2T_x$-Pt-20-400 and K-$Ti_3C_2T_x$-Pt-20 . (I, j) XPS of the C 1s and Ti 2p spectra of TBA-$Ti_3C_2T_x$-Pt-20.

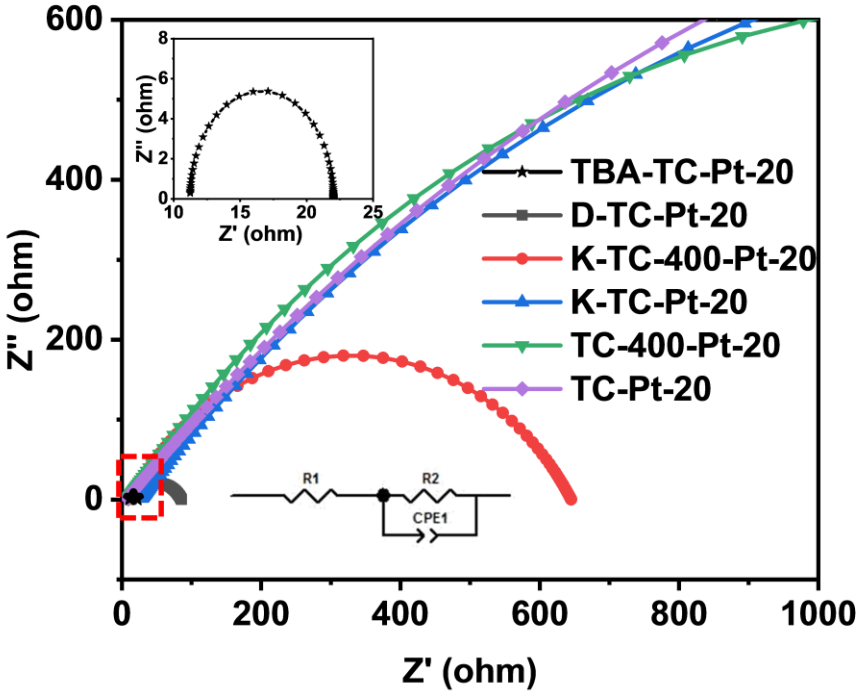



**Figure S9.** The Nyquist plots of the corresponding samples measured at a voltage of -60 mV (vs. the RHE) over the frequency range from 100 kHz to 0.1Hz with the amplitude of 5 mV in 0.5 M $H_2SO_4$.

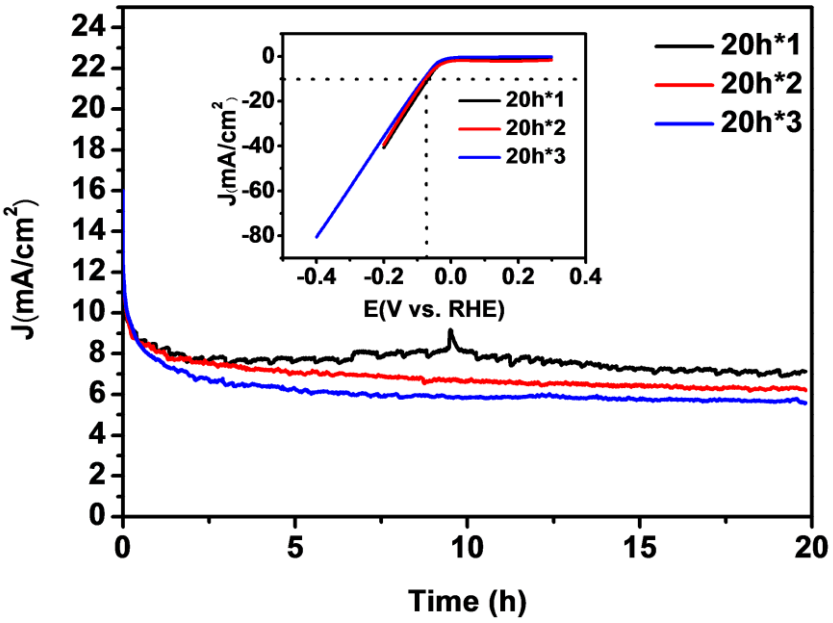



**Figure S10.** The cycles of i-t curves for another 60 h (the total time is 80 h) and the inset is the polarization curves after the corresponding i-t test.

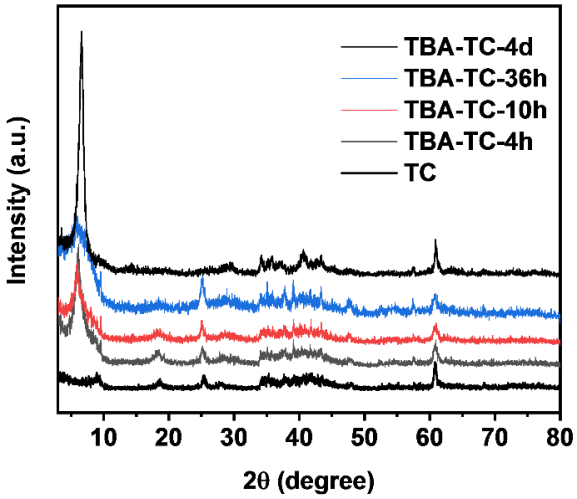



**Figure S11.** Time optimization results in the synthesis of TBA-$Ti_3C_2T_x$

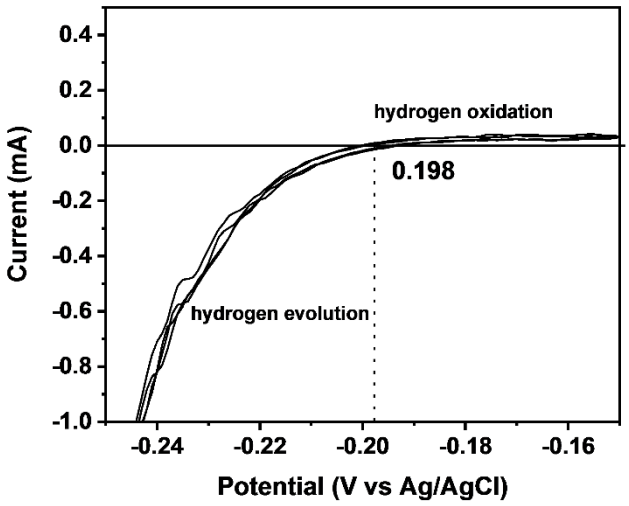



**Figure S12.** The calibration of 3.5 M Ag/AgCl electrode with respect to reversible hydrogen electrode

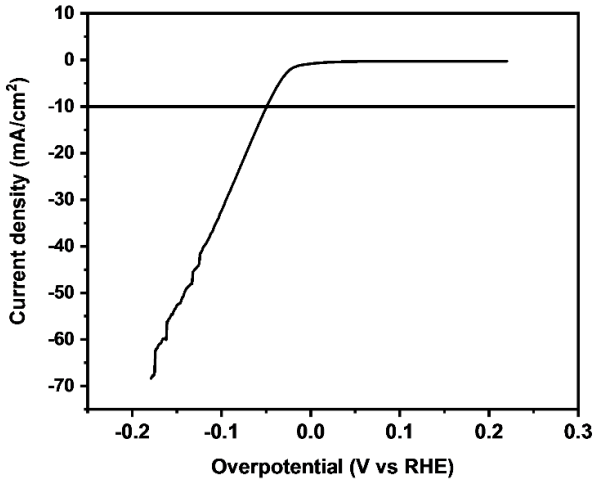



**Figure S13.** The LSV curve of TBA-$Ti_3C_2T_x$-Pt-20 synthesized with short time (12h)

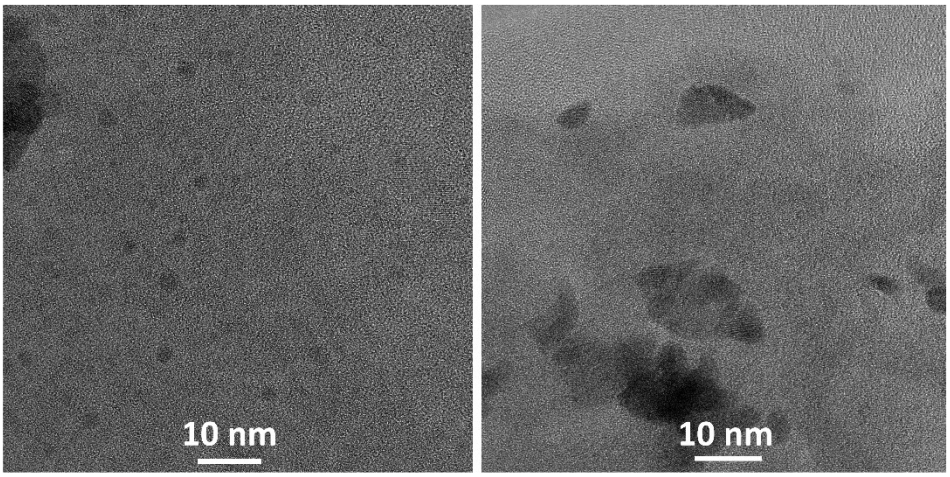



**Figure S14.** HRTEM of TBA-$Ti_3C_2T_x$-Pt-20 before (left) and after (right) cycled for 80 h

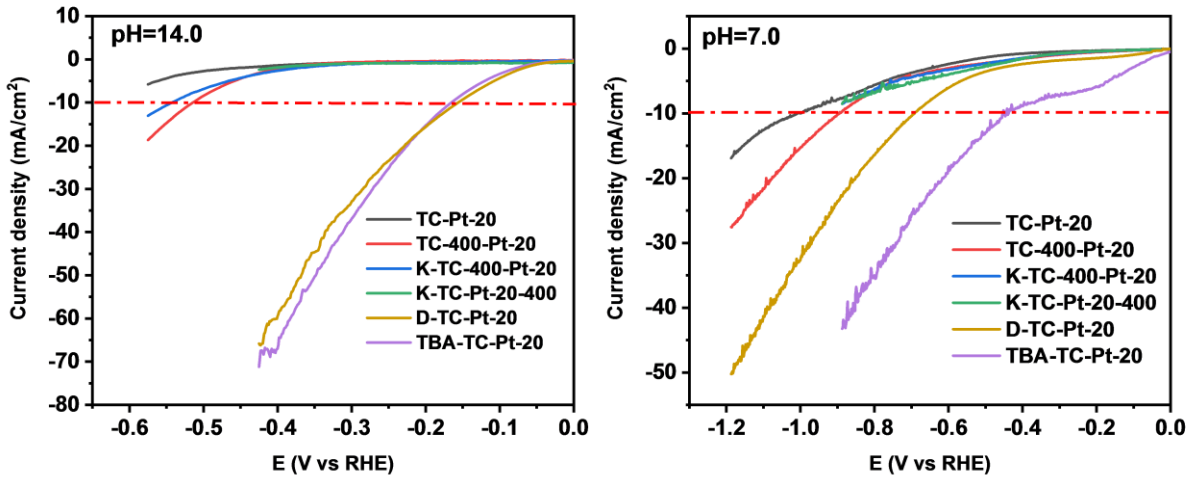



**Figure S15.** Polarization curves of Pt deposited on the supports in 1M KOH (left) and 0.1 M PBS solutions (right).

**Table S1.** Contents of Pt in the catalysts determined by ICP-OES

| Samples | Pt content (wt%) | Pt NPs size* |
|---|---|---|
| TC-400-Pt-20 | 2.3 | -- |
| K-TC-400-Pt-20 | 0.67 | -- |
| K-TC-Pt-20-400 | 1.15 | -- |
| D-TC-Pt-20 | 0.76 | 6.4 nm |
| TBA-TC-Pt-20 | 1.2 | 9.4 nm |
| TBA-TC-Pt-10 | 1.0 | 8.4 nm |
| TBA-TC-Pt-5 | 0.8 | 7.3 nm |
| TBA-TC-Pt-2 | 0.4 | -- |
| TBA-TC-Pt-1 | 0.4 | -- |

* Pt NPs size was calculated by scherrer formula with the XRD data.