

Electronic Supplementary Information

Hydrogen Evolution Reaction in Acidic Media on Single-Crystalline Titanium Nitride Nanowires as an Efficient Non-Noble Metal Electrocatalyst

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Experimental

Preparation of D301-Co-Ti precursor powders

Ion exchange resin was pretreated before used: Macroreticular weak basic styrene type anion exchange resin (10 g, D301, AR, > 99%, Shanghai Hualing Co. Ltd., China) was successively washed with 1 M HCl and 1 M KOH and finally deionized(DI) water to pH=7 to remove the impurities, the as washed resin was then dried at 60 °C. The dried resin was then smashed into powders. 5 g of the as pretreated resin D301 was then added into 100 mL of 0.1 mol L⁻¹ Na₃Co(NO₂)₆·0.5H₂O (Aladdin Chemistry Co. Ltd., China) solution and stirred at 60 °C for 8 h, then dried at 80 °C for 24 h, the color of resin powders will turn from white to light brown(Figure S4(a,b)), revealing that the resin has been exchange or adsorbed with Co(NO₂)₆³⁻ ions(D301-Co).Then the D301-Co powders was mixed with 10 g K₂TiF₆ (Aladdin Chemistry Co. Ltd., China) into 100 mL DI water and stirred at 80 °C for 8 h,then dried at 80 °C for 24 h. The color of resin powders will turn from light brown to light pink (Figure S4c), revealing that the resin has been exchange or adsorbed with TiF₆²⁻ ions as well as Co(NO₂)₆³⁻ ions (D301-Co-Ti), respectively.

Synthesis of TiN NWs

5 g of the as prepared resin D301-Co-Ti powder was then evenly put into a 1.5 cm×3 cm×6 cm graphite boat and then a 1 cm×7 cm graphite bar was placed on top of the graphite boat, then heat treated in a 5 cm diameters tube furnace at 1200 °C for 2 h at a heating rate of 5 °C min⁻¹ in N₂ atmosphere (showed in Figure S5), N₂ gas was kept at a steady flow rate of 150 ml min⁻¹.After cooling down to room temperature, the resulting golden brown TiN nanowires was carefully collected from the surface of the graphite bar and washed in 1M HCl solution with ultrasonic treatment for 5 h to remove impurities, and then washed with DI water several times by centrifugation and dried in an electric oven at 60 °C for 5 h.

Physical Characterization

X-ray diffraction (XRD) was performed on a D-MAX 2200 VPC X-ray diffractometer (Rigaku Co., Japan) with Cu K α radiation source (30 kV and 30 mA) at a scanning rate of 10° min⁻¹. X-ray photoelectron spectroscopy (XPS) measurements were performed in an ESCALAB 250 spectrometer under vacuum (about 2×10⁻⁹ mbar). Monochromatic Al K α (150 W, 1486.6 eV) was used as the excitation source. All the binding energies were calibrated with respect to C 1s peak at 284.8 eV. Scanning electron microscopy (SEM) images were taken with a Quanta 400 FEG scanning electron microscope (FEI company). Transmission electron microscopy (TEM) and EELS investigations were carried out on a FEI Tecnai G2 F30 operating at 300 kV.

Electrochemical Measurements

TiN nanowires (5 mg) and 0.1 mL Nafion solution (5 wt %, DuPont,USA) were mixed with 2.4 mL ethanol with the assistance of sonication (at least 30 min) to form a homogeneous ink, 50 μ L of the catalyst ink were loaded onto a glassy carbon electrode with a diameter of 5 mm (catalyst loading of 0.51 mg cm⁻²). Commercial Bulk TiN electrode was prepared in the same way as TiN NWs electrode. Pt/C (5 mg, 46.7%, TKK, Japan) was mixed with 2.4 mL ethanol and 0.1 mL Nafion solution (5 wt%, DuPont, USA)

with the assistance of sonication (at least 30 min) to form a homogeneous ink. 10 μL of the catalyst ink were loaded onto a glassy carbon electrode with a diameter of 5 mm (catalyst loading of 0.1 mg cm^{-2}). All electrochemical measurements were carried out on an Autolab(AUT85443) in a standard three-electrode system with a reversible hydrogen electrode (RHE) as the reference electrode, and a graphite rod as the counter electrodes, respectively. The electrochemical tests were performed in 1 M HClO_4 solution at a scan rate of 5 mV s^{-1} at $25 \text{ }^\circ\text{C}$.

SEM images of commercial TiN

The SEM image of commercial TiN shows bulky and irregular morphologies, in sharp contrast to the TiN NWs(Figure 1a and 1b) synthesized by our method.

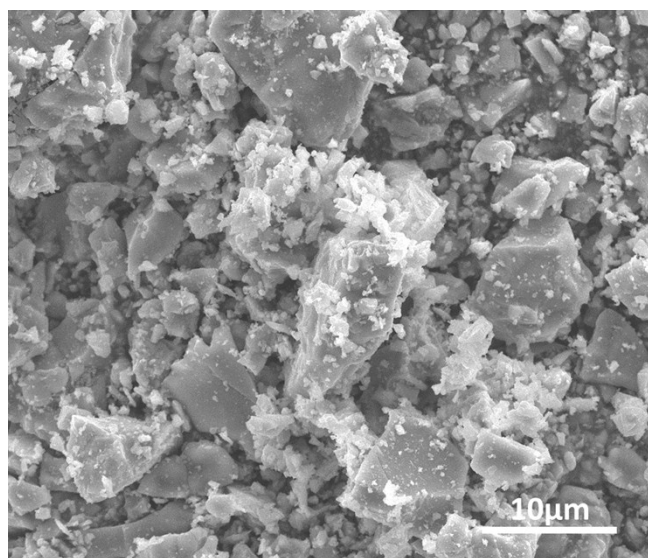


Figure S1. SEM images of commercial bulk TiN nanoparticles.

Equivalent electrical circuit

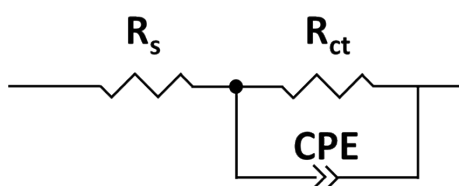


Figure S2. Equivalent electrical circuit used to model the HER process on TiN NW at various overpotentials.

Synthetic Setup

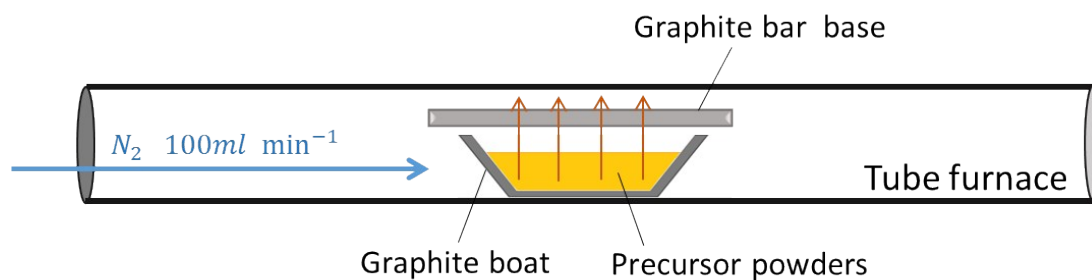


Figure S3. Growth details illustration of TiN nanowires.

Changes of precursor powders in different steps of the synthesis scheme

The color of resin powders will turn from white to light brown (Figure S4(a,b)) after exchanged or adsorbed with $\text{Co}(\text{NO}_2)_6^{3-}$ ions (D301-Co). The color of resin powders will turn from light brown to light pink (Figure S4c) after exchanged or adsorbed with TiF_6^{2-} ions as well as $\text{Co}(\text{NO}_2)_6^{3-}$ ions (D301-Co-Ti). After the heat treatment, the precursor powders will turn to dark brown, revealing the precursor powder have turned to TiN/C, respectively.

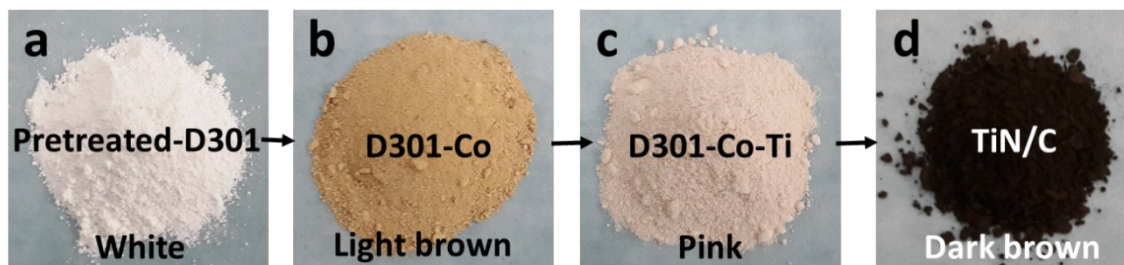


Figure S4. Changes of the precursor powder in the synthesis scheme of TiN nanowires.

TiN NWs could only grow at the temperature above 1200 °C in our experiments. As CVD growth process of the TiN nanowires is difficult to directly observe in situ in the furnace, we investigated it in another way by observing the change of the XRD patterns of the precursor powders annealed at different temperatures ranging from 800 °C to 1200 °C, as showed in figure S5., and the patterns are assigned to PDF cards of different materials. It should be noticed that a series of peaks marked by red asterisks showed in the figure S5 is not in accordance of any known PDF cards to the best of our knowledge, but they are quite similar with the PDF card of $\text{K}_{2.67}\text{TiO}_{0.67}\text{F}_{5.33}$, it's probable that these peaks come from the partially oxidized precursor of K_2TiF_6 , namely $\text{KTi}_x\text{O}_y\text{F}_z$.

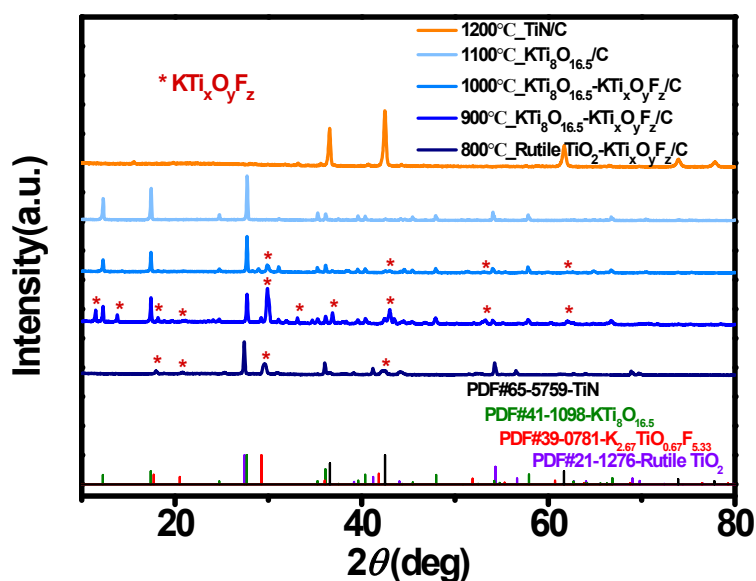


Figure S5. XRD patterns of the precursor powder annealed in N_2 atmosphere at different temperature after acid wash.

We also take a series of comparison experiments to understand the growth mechanism of the TiN NWs. When the exchanged $Co(NO_2)_6^{3-}$ is replaced by $CoCl_2$ in the precursor powders and annealed in N_2 gas, the TiN could still be formed, this result suggest that the N in the $Co(NO_2)_6^{3-}$ is not the main N source in the TiN formation. When annealed in Ar atmosphere instead of N_2 , TiC/C instead of TiN/C was synthesized in the precursor powder, without N_2 gas TiN could not be formed, revealing that N_2 act as the nitrogen source (Figure S6).

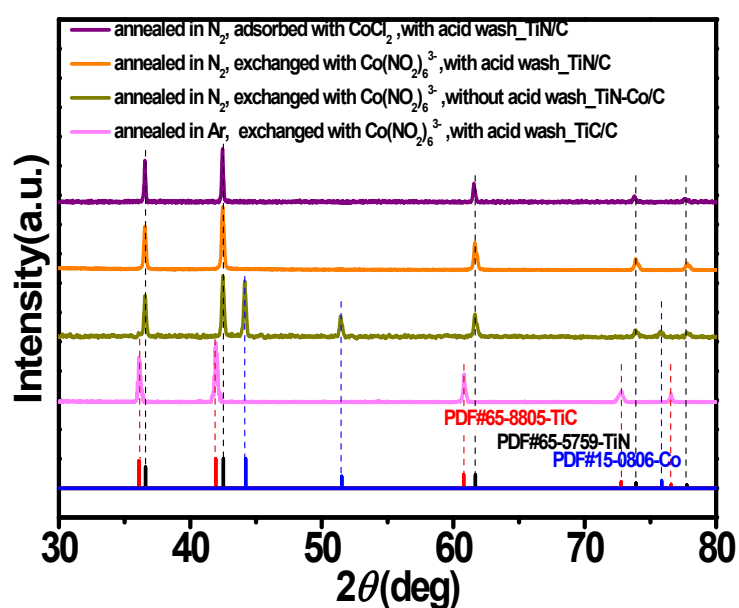
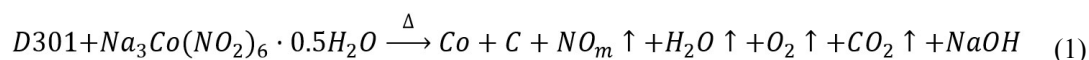


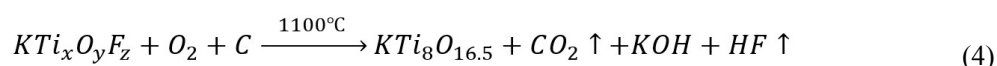
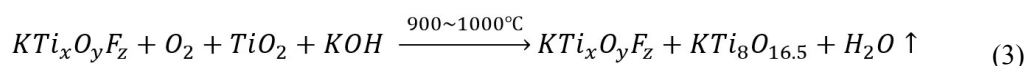
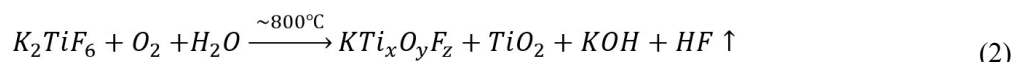
Figure S6. XRD patterns of the precursor powder annealed in different atmosphere with or without acid wash.

Previously works have proved that the ion exchange resin will turn to carbon with the assist of Co catalyst during the heat treatment,¹⁶ The main reactions happened in the heat treatment procedure of precursor powder D301-Co-Ti were considered to be as follow:

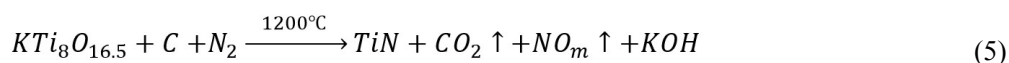
Precursor carbonize step:



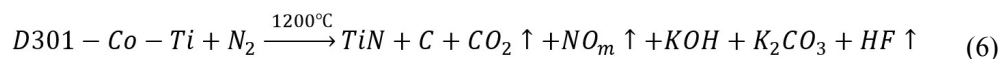
Ti precursor oxidize step:



Ti precursor nitridation step with C as reducing agent:



The whole reaction for the TiN formation can be simplified as the following equation



In fact, these reactions are simplified models that could probably happen, the real reactions of the decomposition of hybrids might be much more complicated.

Effects of the loading amount for the HER performance of the TiN NWs electrode

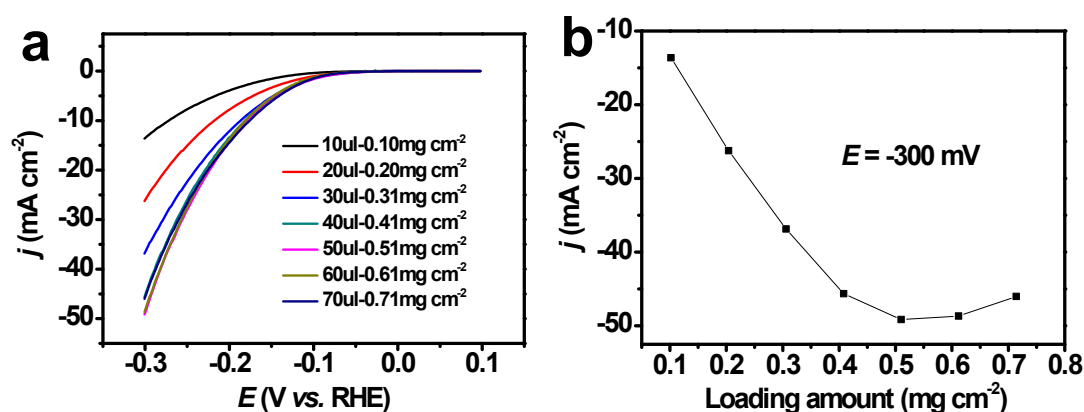


Figure S7.(a)Polarization curves of TiN NWs electrodes of different loading amount. (b)Current density versus loading amount at an applied potential of -300 mV (V vs. RHE).

We've tested a series polarization curves of TiN NWs electrode with different loading amount ranging from 10 μL to 70 μL , as showed in Figure S9, the test shows that the current density at potential of -300 mV increase with the loading amount increase from 10 μL to 50 μL , but decreased at the loading amount of 60 μL and 70 μL ,which suggest that 50 μL (0.51mg cm^{-2}) is an optimal loading amount for the TiN NWs electrode preparation in out experiment.

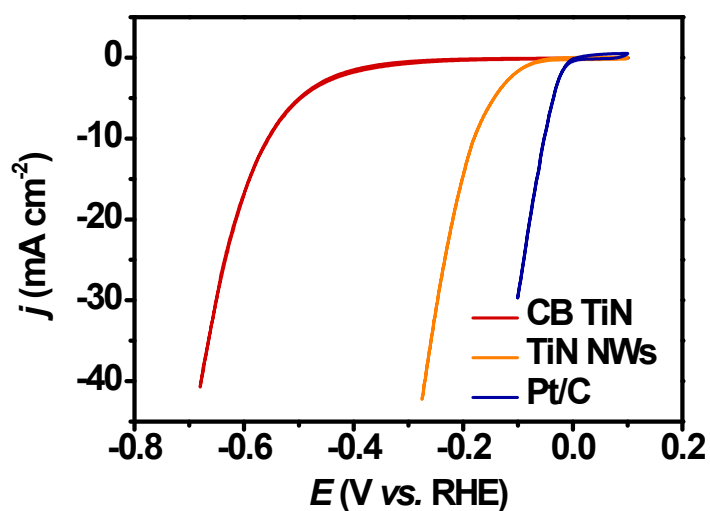


Figure S8. CV curves of the TiN nanowire catalyst along with those of the Pt benchmark catalyst and commercially bulky TiN powders.

Effects of the synthesis temperature for the growth and HER properties of TiN NWs.

We synthesized TiN NWs at 1300 $^{\circ}\text{C}$ and 1400 $^{\circ}\text{C}$ for comparison with TiN NWs grown at 1200 $^{\circ}\text{C}$, and we found that the temperature significantly effect the TiN NWs's morphology and HER performance.

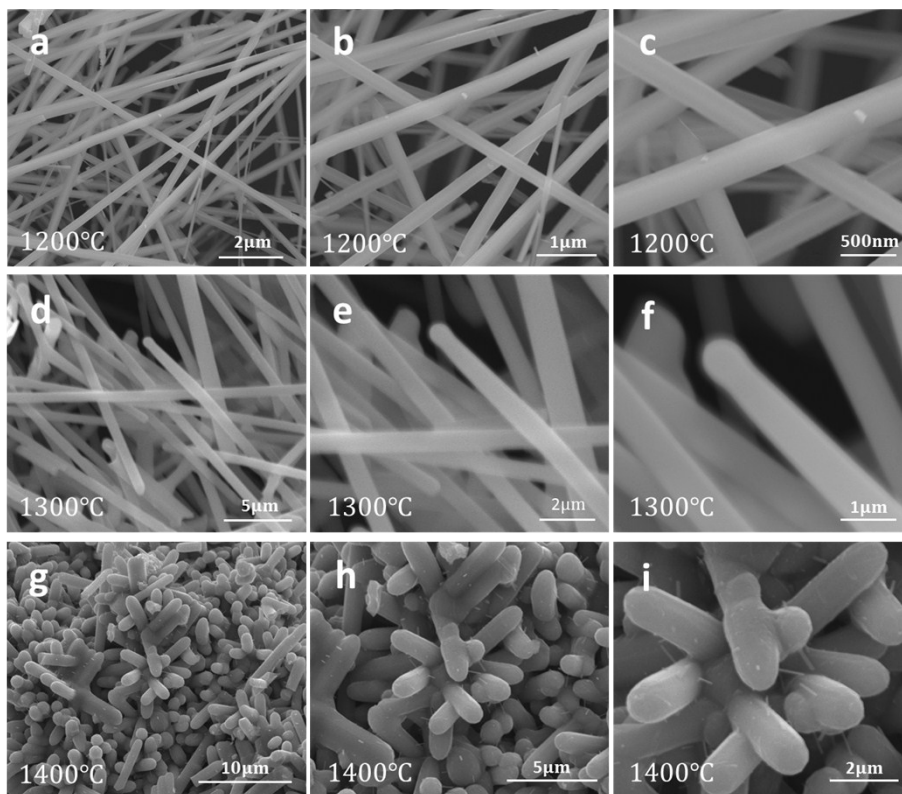


Figure S9. SEM images of TiN NWs synthesized at different temperatures.

At 1200 °C, the TiN NWs possess an average length of 100 μm and diameter of 330 nm, at 1300 °C the average length of TiN NWs decreased to 30 μm and the average diameter increased to 800 nm, at 1400 °C, the average length of TiN NWs decreased to 4 μm and the average diameter increased to 1.1 μm , although we didn't try higher temperature above 1400 °C because of equipment condition limit, the trend of the temperature effect is clear, the higher the synthesis temperature is, the TiN NWs diameter became larger and length became shorter.

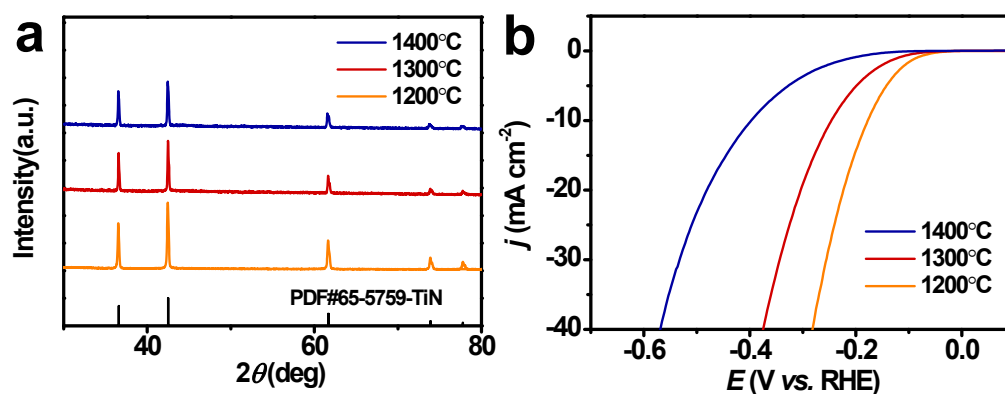


Figure S10.(a)XRD patterns (b)Polarization curves of TiN NWs synthesized at different temperatures.

The HER test reveals that TiN NWs grow at 1200 °C possess the highest activity towards HER, with overpotential of 92 mV at 1 mA cm⁻², TiN NWs grow at 1300 °C display a larger overpotential of 120 mV at 1 mA cm⁻² and TiN NWs grow at 1400 °C display a largest overpotential of 208 mV at 1 mA cm⁻². This result suggest that the TiN NWs with smaller diameter and longer length could offer higher surface area and faster charge transfer rate, which is beneficial for the HER reaction.

Active surface area comparison of TiN NWs and CB TiN

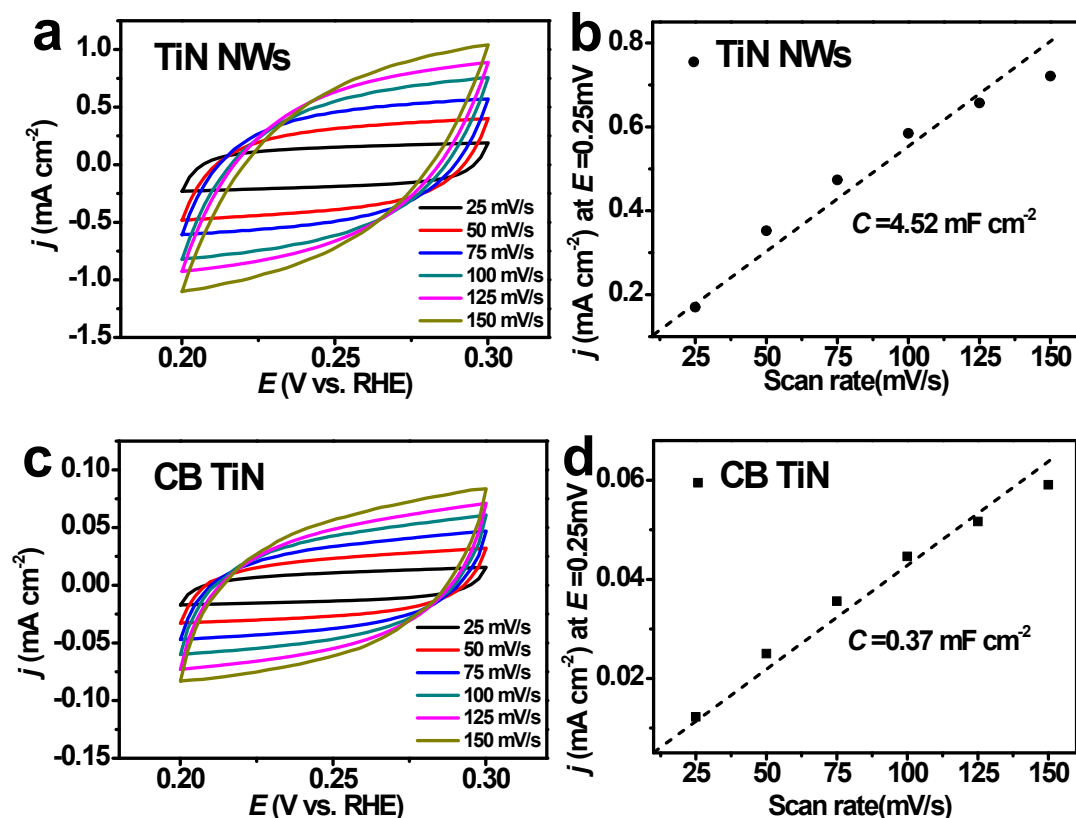


Figure S11. Cyclic voltammograms (CV) curves of (a)TiN NWs and (c)CB TiN taken in a potential window without faradaic processes. The corresponding capacitive currents at 0.25 V vs RHE as a function of scan rate for (b) TiN NWs and (d) CB TiN electrodes.

Table S1. HER performance comparison of different transition metal carbides or nitrides catalysts reported in recent years.

Catalysts	Electrolyte	Current density (mA cm ⁻²)	Corresponding Overpotential (mV)	Tafel slope (mV dec ⁻¹)	References
MoN nanosheets	0.5 M H ₂ SO ₄	onset	100	90	Chem. Sci., 2014, 5 , 4615–4620.
		38.5	300		
WN nanowire array/carbon clothes	0.5 M H ₂ SO ₄	10	198	92	Electrochimica Acta, 2015, 154 , 345–351.
	1 M PBS (pH=7)	2	186	182	
		10	302		
	1 M KOH	2	143	170	
10		285			
Co _{0.6} Mo _{1.4} N ₂	0.1 M HClO ₄	10	200	NA.	J. Am. Chem. Soc., 2013, 135 , 19186–19192.
δ-MoN	0.1 M HClO ₄	5	300		
NiMoN _x /C	0.1 M HClO ₄	onset	78	35.9	Angew. Chem. Int. Ed., 2012, 51 , 6131 – 6135.
MoN/C	0.1 M HClO ₄	onset	157	54.5	
Ta ₃ N ₅ powders	0.1 M H ₂ SO ₄	onset	530	NA.	Applied Catalysis B: Environmental, 2012, 126 , 225–230
		20	763		
TiN powders	0.1 M H ₂ SO ₄	onset	538	NA.	
		20	825		
TiN nanocubes	0.5 M H ₂ SO ₄	1	300	NA.	Journal of Hazardous Materials, 2012, 231–232 , 105–113.
Single-crystalline TiN NWs	1 M HClO ₄	1	92	54	This work.
		40	270		