

# Self-assembled nanodendritic PdPtCu nanosheets/Ti<sub>2</sub>CT<sub>x</sub>-CNT<sub>s</sub> electrocatalysts for low overpotential and long-term stable hydrogen evolution reaction

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## 1. Experimental section

### 1.1 Chemicals and Reagents :

Palladium (II) chloride (PdCl<sub>2</sub>, 99%), chloroplatinic acid hexahydrate (H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O), sulfuric acid (H<sub>2</sub>SO<sub>4</sub>, 98%) were all purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Copric chloride dehydrate (CuCl<sub>2</sub>·2H<sub>2</sub>O), octadecyltrimethylammonium chloride (OTAC) were purchased from Shanghai Macklin Biochemical Co., Ltd. L-Ascorbic acid (AA) was obtained from Alfa Aesar (China) Chemical Co., Ltd. Titanium carbide (Ti<sub>2</sub>CT<sub>x</sub>) MXene multilayer nanosheets were obtained from XFNano Material Technology Co., Ltd. Multiwalled carbon nanotubes (CNTs) was provided from Chendu Chemicals Co., Ltd. Pt/C (20 wt%) and Nafion (5 wt%) were provided from Sigma-Aldrich. Ultra-filtered water (18.2 MΩ·cm) used in the experiments was obtained by a Millipore purification system (Simplicity).

### 1.2 Preparation of PdPtCu nanosheets

Firstly, H<sub>2</sub>PdCl<sub>4</sub> solution was prepared as followed: 1 g PdCl<sub>2</sub>, 1.143 g HCl and 562.857 g ultra-filtered water were mixed in the reagent bottle and then being shaken for 3 h at 60 °C. In a typical synthesis of Pd<sub>35</sub>Pt<sub>19</sub>Cu<sub>46</sub> nanosheets, H<sub>2</sub>PdCl<sub>4</sub> (4 ml, 0.01 M), H<sub>2</sub>PtCl<sub>6</sub> (2 ml, 0.01 M) and CuCl<sub>2</sub> (6 ml, 0.01 M) aqueous solution were sequentially added into OTAC solution (200 ml, 0.01 M), respectively. After mixing homogeneous by bath-sonicated for 15 min, 12 ml of 0.1 M AA was speedily injected into the mixture and kept without agitation at 25 °C for 4 h. The solid products were collected by centrifugation at 11000 rpm for 30 min with water and ethanol. The preparation of Pd<sub>55</sub>Pt<sub>18</sub>Cu<sub>27</sub>, Pd<sub>43</sub>Pt<sub>16</sub>Cu<sub>41</sub> and Pd<sub>24</sub>Pt<sub>11</sub>Cu<sub>65</sub> is in principle the same as that of Pd<sub>35</sub>Pt<sub>19</sub>Cu<sub>46</sub> nanosheets, except that the amount of precursor CuCl<sub>2</sub> (0.01 M) is adjusted to 2 ml, 4 ml and 8 ml. Pd<sub>60</sub>Pt<sub>40</sub> and Pd<sub>59</sub>Cu<sub>41</sub> were synthesized at the same reaction temperature and reaction time, but the nominal molar ratios of Pd<sub>60</sub>Pt<sub>40</sub> and Pd<sub>59</sub>Cu<sub>41</sub> were kept at Pd:Pt = 1:1 and Pd:Cu = 1:1, respectively.

### 1.3 Preparation of Ti<sub>2</sub>CT<sub>x</sub>-CNTs heterostructures

20 mg CNTs were dispersed into 20 ml OTAC (0.01 M) to form OTAC-grafted positively charged CNTs under vigorous sonification for 2 h. Then, 20 mg Ti<sub>2</sub>CT<sub>x</sub> powder was added in 20 ml deionized water and sonicated for 2 h under N<sub>2</sub> flow to obtain the delaminated Ti<sub>2</sub>CT<sub>x</sub>. To prepare Ti<sub>2</sub>CT<sub>x</sub>-CNTs heterostructures, the OTAC-grafted CNTs were added dropwise into negatively charged Ti<sub>2</sub>CT<sub>x</sub> suspension and sonicated for 30 min. Ti<sub>2</sub>CT<sub>x</sub>-CNTs with different compositions (mass ratio = 0.5:1, 1:1, 2:1 and 3:1) can be obtained by varying the starting mass ratio of Ti<sub>2</sub>CT<sub>x</sub> and CNTs.

### 1.4 Preparation of PdPtCu/Ti<sub>2</sub>CT<sub>x</sub>-CNTs electrocatalyst

To obtain typical PdPtCu/Ti<sub>2</sub>CT<sub>x</sub>-CNTs electrocatalysts, the as-synthesized PdPtCu solution was slowly added to the Ti<sub>2</sub>CT<sub>x</sub>-CNTs solution under sonification for 30 min. After that, the PdPtCu/Ti<sub>2</sub>CT<sub>x</sub>-CNTs solution were lyophilized for 2 days to obtain the powder electrocatalysts for HER.

### 1.5 Zeta potential measurements

The zeta potential measurements were conducted using a Zetasizer Nano ZS Malvern Laser Particle Sizer. Before self-assembly, the as-synthesized PdPtCu solution was centrifuged one time to remove the free OTAC from the solution. Afterwards, the supernatant was collected and further diluted to original volume with ultrapure water. And then the solution was sent to self-assembly and zeta potential measurement. As for OTAC-grafted CNTs (CNTs-OTAC), Ti<sub>2</sub>CT<sub>x</sub>, self-assembled Ti<sub>2</sub>CT<sub>x</sub>-CNTs heterostructures (Ti<sub>2</sub>CT<sub>x</sub>-CNTs), PdPtCu/Ti<sub>2</sub>CT<sub>x</sub>, PdPtCu/Ti<sub>2</sub>CT<sub>x</sub>-CNTs samples, the as-prepared solutions were directly sent for zeta potential measurements.

### 1.6 Materials Characterization

The crystal structure was examined using X-ray diffraction by X Pert-Pro MPD diffractometer (Netherlands PANalytical) with a Cu K $\alpha$  X-ray source ( $\lambda = 1.540598 \text{ \AA}$ ). X-ray photoelectron spectroscopy (XPS, hermo Scientific ESCALAB 250 XI X-ray photoelectron spectrometer) was performed to measure the elemental compositions and chemical states in samples. The contents of elemental metals were determined by the inductively coupled plasma optical emission spectrometer (ICP-OES, Varian 710-ES). The Hitachi HT7700 at an acceleration voltage of 120 kV was adopted to collect Low magnification transmission electron microscopy (TEM) images. Scanning Electron Microscope (SEM) images were received from Hitachi SU8010. High resolution TEM (HRTEM) images and energy dispersive X-ray spectroscopy (EDS) elemental mapping were obtained from FEI Tecnai F20 transmission electron microscope at an acceleration voltage of 200 kV. Atomic force microscopy (AFM) image was collected on a Bruker Dimension Icon. Fourier transform infrared attenuated total reflection (FTIR-ATR) spectra were acquired on Nicolet iS20 Fourier transform infrared spectrometer. The zeta potential measurements were made using Zetasizer Nano ZS Malvern Laser Particle Sizer.

## 1.7 Electrochemical Measurements

Electrochemical experiments were performed on a CHI 660E potentiostat at room temperature. The working electrode, reference electrode and counter electrode are glassy carbon electrode (GCE, 3 mm in diameter), saturated calomel electrode (SCE) and graphite rod in turn. For fabricating PdPtCu/Ti<sub>2</sub>CT<sub>x</sub>-CNTs electrocatalyst ink, a certain amount of PdPtCu/Ti<sub>2</sub>CT<sub>x</sub>-CNTs solution with a mass ratio of PdPtCu:Ti<sub>2</sub>CT<sub>x</sub>-CNTs by 1:2 was freeze-dried into PdPtCu/Ti<sub>2</sub>CT<sub>x</sub>-CNTs powder. Afterwards, 3 mg powder was dispersed into a solution containing 400  $\mu\text{l}$  H<sub>2</sub>O, 560  $\mu\text{l}$  ethanol and 40  $\mu\text{l}$  Nafion solution and then subjected to vigorous ultrasonication for 30 min to form a uniform ink. For other catalysts, we also kept the mass ratio of nanoalloys and catalyst supports unchanged at 1:2. As for Pt/C catalyst, 3 mg 20 wt% commercial Pt/C was weighed. The Pd +Pt loadings of all catalysts on the GCE have been listed in Table S2. Subsequently, 5  $\mu\text{l}$  of the electrocatalyst ink was drop-cast on the GCE and dried naturally in the air. Before HER measurements, the electrolyte was bubbled with N<sub>2</sub> for at least 30 min to remove residual O<sub>2</sub>. Linear sweep voltammetry (LSV) curves were tested at a scan rate of 5 mV s<sup>-1</sup> in the 0.5 M H<sub>2</sub>SO<sub>4</sub> electrolyte, and obtained with 50% iR compensations through instrument automatic settings. All recorded potentials (overpotentials) were converted to the reversible hydrogen electrode (RHE).

CO stripping measurements were used to estimate the electrochemical active surface area (ECSAs) of electrocatalysts by integrating the carbon monoxide oxidation charge. First, we kept the potential at 0.05 V<sub>RHE</sub> for 10 min in a CO-saturated 0.5 M H<sub>2</sub>SO<sub>4</sub> electrolyte. Then, N<sub>2</sub> was purged for 30 min to remove CO from electrolyte. Immediately afterward, CV cycles were performed with a scan rate of 50 mV s<sup>-1</sup> for at least two consecutive cycles. The ECSAs of a catalyst was estimated by the following formula:

$$ECSA = \frac{Q_{CO}}{C \times m_{Pd+Pt}}$$

where Q<sub>CO</sub> is the charge calculated for the oxidation of the adsorbed CO (CO<sub>ads</sub>) on the catalyst, C (420  $\mu\text{C cm}^{-2}$ ) is the charge needed to oxidize a monolayer of CO<sub>ads</sub>, and m<sub>Pd+Pt</sub> is the mass of the Pd+Pt loading on the electrode surface.

Cycle stability of catalysts was performed by continuous potential sweeps between -0.15 and 0.15 V versus RHE at a scan rate of 100 mV s<sup>-1</sup>. The long-term durability of all electrocatalysts was examined by potentiostatic electrolysis at an overpotential with the current density of 10 mA cm<sup>-2</sup>. Electrochemical impedance spectra (EIS) measurements were carried out at 0 V vs RHE from 10<sup>5</sup> Hz to 0.1 Hz at an amplitude of 5 mV.

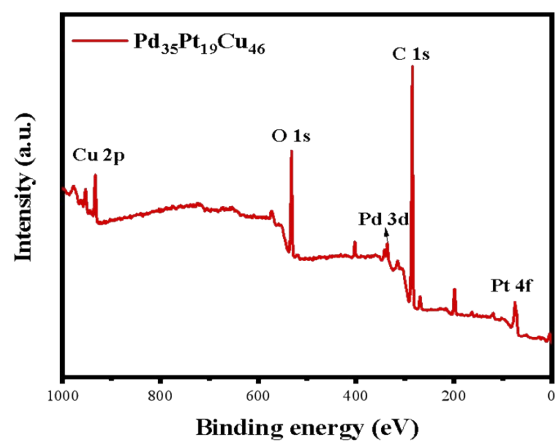


Fig. S1 XPS survey spectrum of Pd<sub>35</sub>Pt<sub>19</sub>Cu<sub>46</sub> nanosheets.

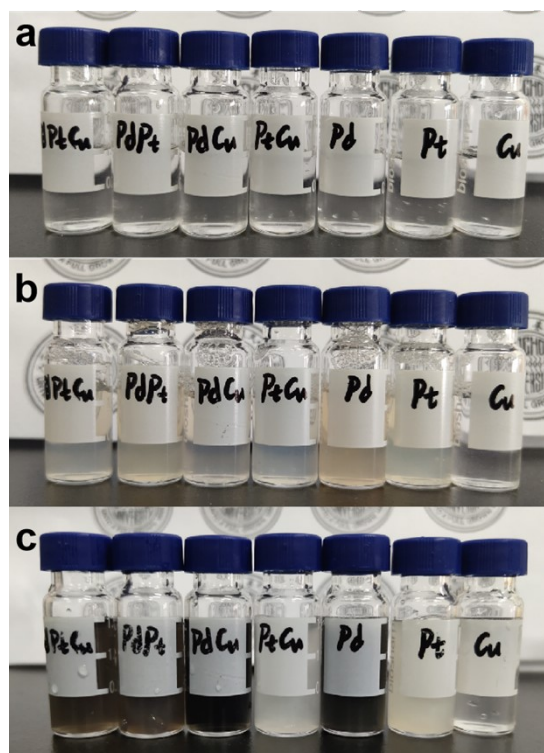
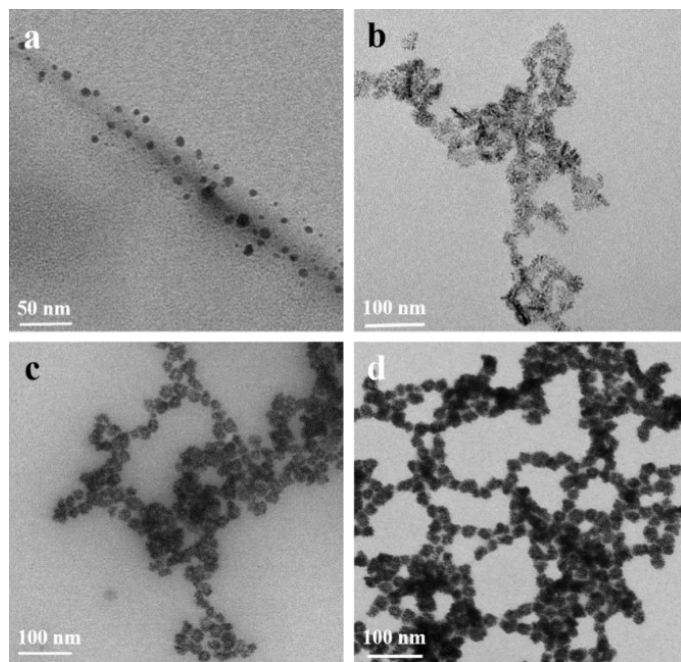
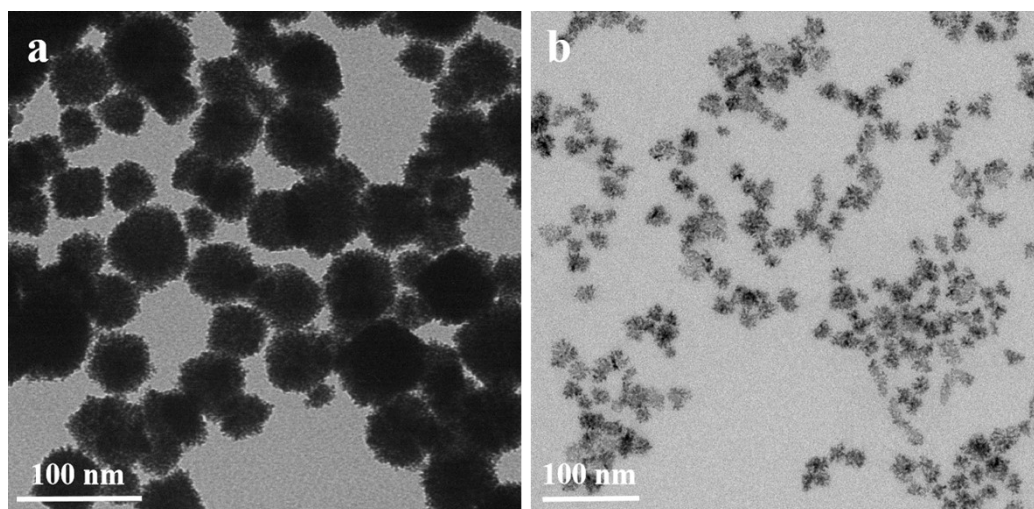


Fig. S2 Photographs of OTAC solutions containing various precursors (From left to right: PdPtCu, PdPt, PdCu, PtCu, Pd, Pt and Cu): Pd stands for H<sub>2</sub>PdCl<sub>4</sub>, Pt stands for H<sub>2</sub>PtCl<sub>6</sub> and Cu stands for CuCl<sub>2</sub>. (a) Pure OTAC solutions without metal precursors; (b) after further adding various precursors according to the marks; (c) after adding AA and reacted at 25 °C for 4 h.



**Fig. S3** TEM images of PdPtCu nanoalloys reacted at different temperature. (a) 10 °C ; (b) 25 °C ; (c) 40 °C and (d) 60 °C .



**Fig. S4** TEM images of PdPtCu reacted in (a) Ultra-filtered water; (b) 0.01M OTAC solution 25 °C for 4 h.

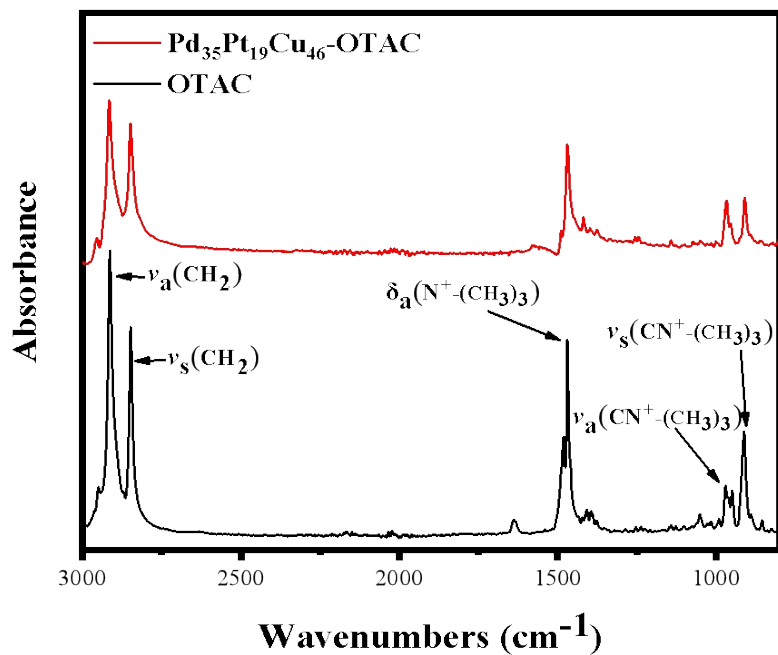


Fig. S5 FTIR spectra of OTAC and PdPtCu-OTAC.

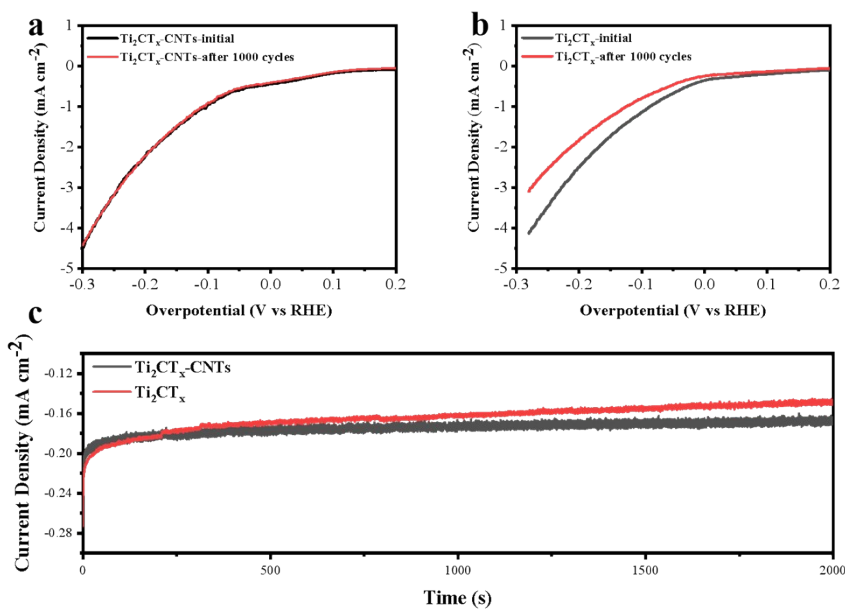
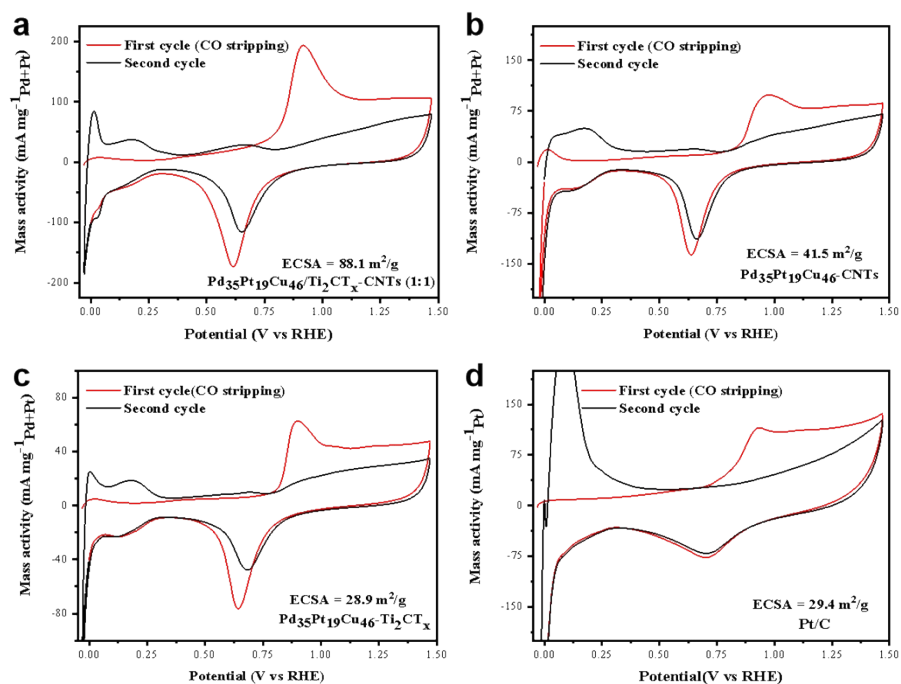
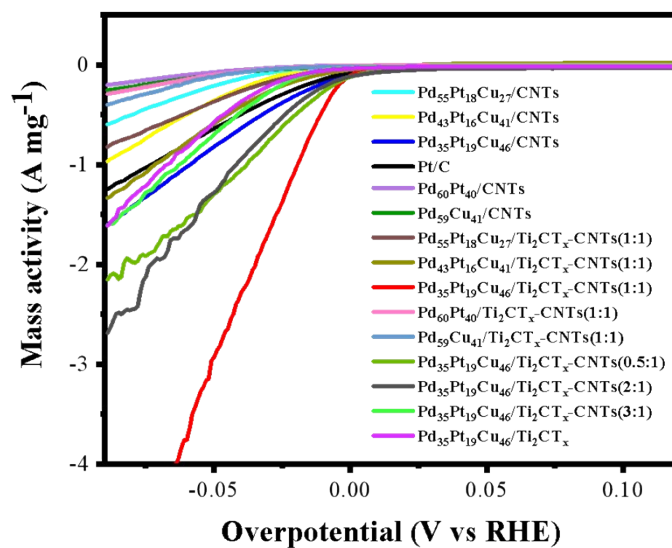


Fig. S6 (a-b) LSV curves and durability test between  $-0.25 \sim 0.15$  V vs RHE of  $\text{Ti}_2\text{CT}_x$ -CNTs heterostructure and  $\text{Ti}_2\text{CT}_x$  in  $0.5\text{M H}_2\text{SO}_4$  at a scan rate of  $5 \text{ mV s}^{-1}$ . (c) Chronoamperometry measurement at an overpotential with the current density of  $0.2 \text{ mA cm}^{-2}$  for 2000s for  $\text{Ti}_2\text{CT}_x$ -CNTs heterostructure ( $-0.053$  V vs RHE) and  $\text{Ti}_2\text{CT}_x$  ( $-0.061$  V vs RHE).



**Fig. S7** (a-d) CO stripping tests of Pd<sub>35</sub>Pt<sub>19</sub>Cu<sub>46</sub>/Ti<sub>2</sub>CT<sub>x</sub>-CNTs, Pd<sub>35</sub>Pt<sub>19</sub>Cu<sub>46</sub>/CNTs, Pd<sub>35</sub>Pt<sub>19</sub>Cu<sub>46</sub>/Ti<sub>2</sub>CT<sub>x</sub> and Pt/C in N<sub>2</sub> purged 0.5 M H<sub>2</sub>SO<sub>4</sub>, recorded at 50 mV s<sup>-1</sup>.



**Fig. S8** LSV curves of different catalysts based on Pd + Pt mass loading in 0.5 M H<sub>2</sub>SO<sub>4</sub> at a scan rate of 5 mV s<sup>-1</sup>.

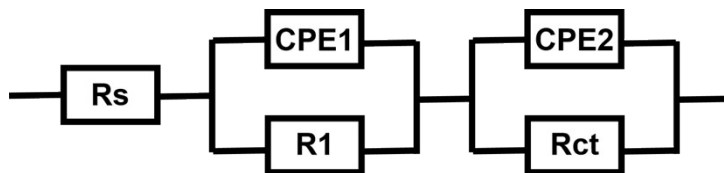


Fig. S9 The 2CPE equivalent circuit.

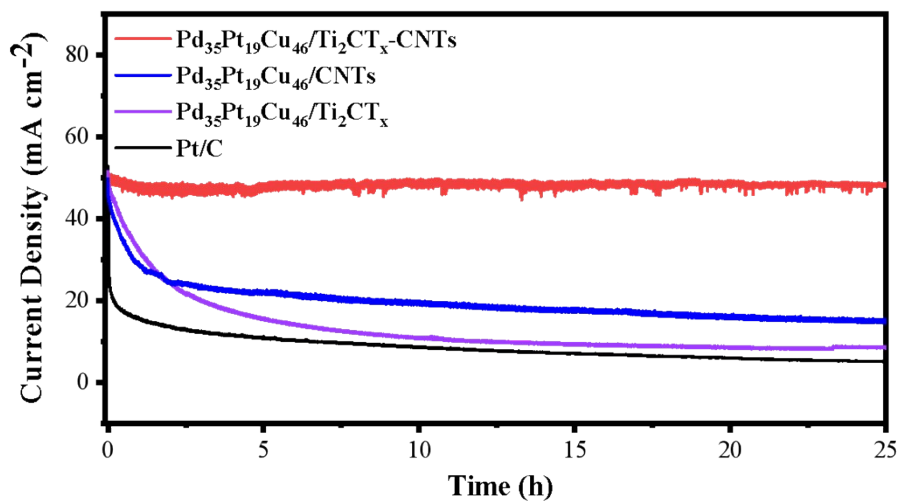


Fig. S10 Chronoamperometry measurement at an overpotential with the current density of 50 mA cm<sup>-2</sup> for 25 h for Pd<sub>35</sub>Pt<sub>19</sub>Cu<sub>46</sub>/Ti<sub>2</sub>CT<sub>x</sub>-CNTs (-0.019 V vs RHE), Pd<sub>35</sub>Pt<sub>19</sub>Cu<sub>46</sub>/CNTs (-0.057 V vs RHE), Pd<sub>35</sub>Pt<sub>19</sub>Cu<sub>46</sub>/Ti<sub>2</sub>CT<sub>x</sub> (-0.066 V vs RHE) and Pt/C (-0.063 V vs RHE).

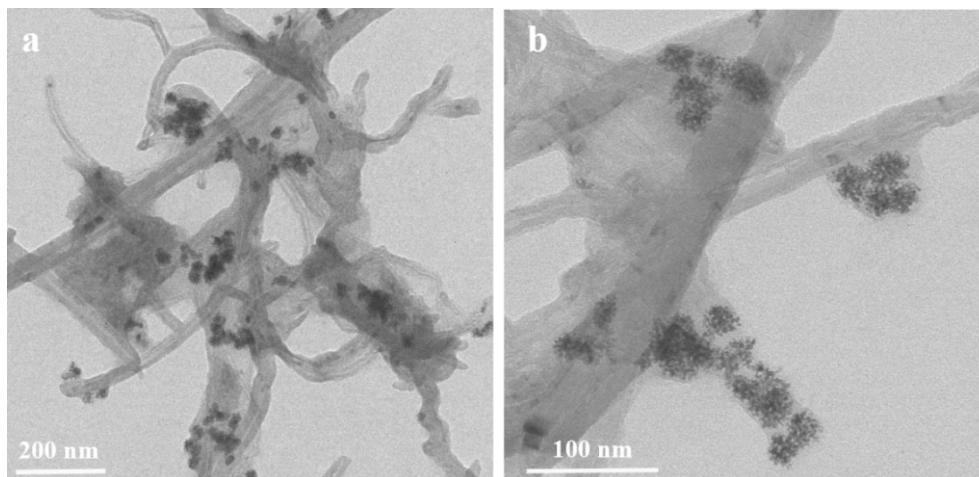


Fig. S11 (a-b) TEM images of Pd<sub>35</sub>Pt<sub>19</sub>Cu<sub>46</sub>/Ti<sub>2</sub>CT<sub>x</sub>-CNTs (1:1) electrocatalyst obtained after 25 h HER electrochemical test.

**Table S1.** Summary of ICP results and corresponding atomic ratios of different electrocatalysts

Electrocatalysts	Pd at%	Pt at%	Cu at%
Pd <sub>2</sub> Pt <sub>1</sub> Cu <sub>1</sub>	55	18	27
Pd <sub>2</sub> Pt <sub>1</sub> Cu <sub>2</sub>	43	16	41
Pd <sub>2</sub> Pt <sub>1</sub> Cu <sub>3</sub>	35	19	46
Pd <sub>2</sub> Pt <sub>1</sub> Cu <sub>4</sub>	24	11	65
Pd <sub>1</sub> Pt <sub>1</sub>	60	40	/
Pd <sub>1</sub> Cu <sub>1</sub>	59	/	41

**Table S2.** Summary of Pd + Pt mass loadings of all investigated catalysts

Catalyst	Pd + Pt mass loading ( $\mu\text{g}_{\text{Pd+Pt}} \text{cm}^{-2}$ )
Pd <sub>55</sub> Pt <sub>18</sub> Cu <sub>27</sub> /CNTs	52.14
Pd <sub>43</sub> Pt <sub>16</sub> Cu <sub>41</sub> /CNTs	42.14
Pd <sub>35</sub> Pt <sub>19</sub> Cu <sub>46</sub> /CNTs	38.57
Pd <sub>60</sub> Pt <sub>40</sub> /CNTs	71.43
Pd <sub>59</sub> Cu <sub>41</sub> /CNTs	21.14
Pd <sub>55</sub> Pt <sub>18</sub> Cu <sub>27</sub> /Ti <sub>2</sub> CT <sub>x</sub> -CNTs (1 : 1)	52.14
Pd <sub>43</sub> Pt <sub>16</sub> Cu <sub>41</sub> /Ti <sub>2</sub> CT <sub>x</sub> -CNTs (1 : 1)	42.14
Pd <sub>35</sub> Pt <sub>19</sub> Cu <sub>46</sub> /Ti <sub>2</sub> CT <sub>x</sub> -CNTs (1 : 1)	38.57
Pd <sub>60</sub> Pt <sub>40</sub> /Ti <sub>2</sub> CT <sub>x</sub> -CNTs (1 : 1)	71.43
Pd <sub>59</sub> Cu <sub>41</sub> /Ti <sub>2</sub> CT <sub>x</sub> -CNTs (1 : 1)	42.14
Pd <sub>35</sub> Pt <sub>19</sub> Cu <sub>46</sub> /Ti <sub>2</sub> CT <sub>x</sub> -CNTs (0.5 : 1)	38.57
Pd <sub>35</sub> Pt <sub>19</sub> Cu <sub>46</sub> /Ti <sub>2</sub> CT <sub>x</sub> -CNTs (2 : 1)	38.57
Pd <sub>35</sub> Pt <sub>19</sub> Cu <sub>46</sub> /Ti <sub>2</sub> CT <sub>x</sub> -CNTs (3 : 1)	38.57
Pd <sub>35</sub> Pt <sub>19</sub> Cu <sub>46</sub> /Ti <sub>2</sub> CT <sub>x</sub>	38.57
Pt/C	39.71



**Table S3.** Summary of the overpotential and Tafel slope of Pd<sub>35</sub>Pt<sub>19</sub>Cu<sub>46</sub>/Ti<sub>2</sub>CT<sub>x</sub>-CNTs (1:1) and recently reported noble metal or noble metal-based electrocatalysts in acidic electrolyte

Electrocatalysts	Electrolyte	Overpotential <sub>j=10 mA cm<sup>-2</sup></sub> (mV)	Tafel slope (mV dec <sup>-1</sup> )	Reference
Pd <sub>35</sub> Pt <sub>19</sub> Cu <sub>46</sub> /Ti <sub>2</sub> CT <sub>x</sub> -CNTs	0.5M H <sub>2</sub> SO <sub>4</sub>	4	18	This work
Pt/Ti <sub>3</sub> C <sub>2</sub> T <sub>x</sub> -550	0.1M HClO <sub>4</sub>	33	32	Ref.[1]
Pt <sub>3.21</sub> Ni@Ti <sub>3</sub> C <sub>2</sub>	0.5M H <sub>2</sub> SO <sub>4</sub>	19	13	Ref.[2]
PtO <sub>a</sub> PdO <sub>b</sub> NPs@Ti <sub>3</sub> C <sub>2</sub> T <sub>x</sub>	0.5M H <sub>2</sub> SO <sub>4</sub>	27	39	Ref.[3]
TBA-Ti <sub>3</sub> C <sub>2</sub> T <sub>x</sub> -Pt-20	0.5M H <sub>2</sub> SO <sub>4</sub>	55	65	Ref.[4]
MXene/Pt-3	0.5M H <sub>2</sub> SO <sub>4</sub>	302	79	Ref.[5]
40Pt-TBA-Ti <sub>3</sub> C <sub>2</sub> T <sub>x</sub>	0.5M H <sub>2</sub> SO <sub>4</sub>	68	70	Ref.[6]
Mo <sub>2</sub> TiC <sub>2</sub> T <sub>x</sub> -Pt <sub>5A</sub>	0.5M H <sub>2</sub> SO <sub>4</sub>	30	30	Ref.[7]
Pt-MXene-CNTs	0.5M H <sub>2</sub> SO <sub>4</sub>	62	78	Ref.[8]
Pd/Nb <sub>2</sub> C-HF	0.5M H <sub>2</sub> SO <sub>4</sub>	34	34	Ref.[9]
2.4% Pt@mh-3D MXene	0.5M H <sub>2</sub> SO <sub>4</sub>	13	24	Ref.[10]
Ru <sub>5A</sub> -N-S-Ti <sub>3</sub> C <sub>2</sub> T <sub>x</sub>	0.5M H <sub>2</sub> SO <sub>4</sub>	76	90	Ref.[11]
Ru <sub>5A</sub> -N-Ti <sub>3</sub> C <sub>2</sub> T <sub>x</sub>	0.5M H <sub>2</sub> SO <sub>4</sub>	23	42	Ref.[12]

**Notes and References:**

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