## Directly Immobilizing Ru-Tannic Acid linkage coordination Complex on Carbon Cloth: An Efficient and Ultrastable Catalyst for Hydrogen Evolution Reaction

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## Materials and methods

**Materials:** Ruthenium(III) chloride anhydrous (RuCl<sub>3</sub>), tannic acid (TA) and sodium borohydride (NaBH<sub>4</sub>) were purchased from Aladdin Inc. Carbon cloth was purchased from Shanghai Hesen Electric Co. Ltd.

**Preparation of Ru-TA/ACC:** Typically, 1×4 cm<sup>2</sup> ACC was sonicated in deionized water for 10 min and ethanol for 10 min in sequence to remove impurities. Then, the ACC was placed in 20 mL water with ultrasound treatment for 10 min. Next, 50 uL RuCl<sub>3</sub> solution (0.048 M) was added dropwise into the 20 mL water with ultrasonic treatment for 10 min. After that, 5 mL TA aqueous solution (0.002 M) and 200 uL 1.0 M KOH solution was dropwise added into the solution in sequence under ultrasonic treatment. After 10 min, the obtained Ru-TA/ACC was washed with ultrapure water and ethanol several times, respectively, and then dried under vacuum at 50 °C for 18h.

**Preparation of Ru/ACC:** Firstly,  $1 \times 4$  cm<sup>2</sup> ACC were ultrasonicated for 10 min in ultrapure water and ethanol in sequence to remove impurities. And then the ACC was placed in 20 mL water with ultrasound treatment for 10 min. Next, 50 uL RuCl<sub>3</sub> solution (0.048 M) was dropwise added into the 20 mL water with ultrasonic treatment for 10 min. After that, 30 mg NaBH<sub>4</sub> was slowly added into the above solution with ultrasound treatment for 20 min. Finally, the obtained Ru/ACC was washed with ultrapure water and ethanol several times and then dried under vacuum at 50 °C for 18h.

**Preparation of activated carbon cloth (ACC):** Briefly, a piece of carbon cloth (CC, HCCP330, Shanghai Hesen Electric Co. Ltd., China) was washed with ethanol and dried before use. Then, CC was annealed at 600 °C for 1h in nitrogen (99.99%, 280 sccm) with a heating rate of 10 °C min<sup>-1</sup> and then cooled to room temperature. Then the ACC was collected and used as carbon substrate.

**Characterization:** Scanning electron microscope (SEM) was performed on SU-70 microscope. The high-resolution TEM (HRTEM), HADDF-STEM and EDS mapping were carried out on the JEOL JEM-2100F. Spherical aberration corrected Transmission Electron Microscope was performed on a FEI Titan G2 80-200 ChemiSTEM at an acceleration voltage of 200 kV. Power X-ray diffraction (XRD) patterns were recorded on a Rigaku Ultima IV operating at 40 kV and 20 mA with Cu Kα radiation. Electron paramagnetic resonance (EPR) measurement was performed on a Bruker A300 EPR Spectrometer at room temperature. The inductively coupled plasma-atomic emission spectrometry (ICP-AES) was carried out on a Perkin Elmer Optima OES 800. The X-ray photoelectron spectra (XPS) was recorded on an Escalab 250Xi spectrometer. Raman spectra was obtained using a LabRam HRUV.

**Electrochemical measurement:** electrochemical performance was evaluated on CHI 760E electrochemical workstation in a three-electrode system. Samples were cut into  $1 \times 1 \text{ cm}^2$  square and directly used as the working electrode. A graphite rod and asaturated calomel electrode (SCE) were used as the counter electrode and the reference electrode, respectively. All the potentials vs. SCE was converted to the reversible hydrogen electrode (RHE) using the equation  $E_{vs RHE} = E_{vs SCE} + E^0_{SCE} + 1.982 \times 10^{-4} \times T \times pH$  (T is Kelvin temperature). Linear sweep voltammetry was carried out in 1.0 M KOH, 1.0 M PBS and 0.5 M H<sub>2</sub>SO<sub>4</sub> at a scan rate of 2 mV/s. Electrochemical impedance spectroscopy (EIS) measurements were performed from 100 kHz to 0.01 Hz with an amplitude of 5 mV at an overpotential of 100 mV vs. RHE in 1.0 M KOH solution. All the polarization curves are the steady ones after several scans. And all polarization curves were plotted without IR compensation. The electrochemical double-layer capacitances (CdI) of materials were obtained at non-Faradaic current area. By plotting the current density between anode and cathode (J<sub>anodic</sub>-J<sub>cathodic</sub>) against scan rates at 0.15

V vs. RHE, half of the fitting line slope is equal to geometric double layer capacitance. **Active sites measurements:** The underpotential deposition (UPD) has proven to be an ideal method to qualify active sites for Ru. In a 0.5 M H<sub>2</sub>SO<sub>4</sub> + 20 mM CuSO<sub>4</sub> + 60 mM NaCl solution, peaks of UPD, OPD and the corresponding stripping are distinct in CV curves. Then, LSV was performed at an initial overpotential from 0.175 to 0.265 V to strip Cu. And the charges obtained from the stripping of the aforementioned UPD Cu are plotted. The platform in the middle potential region is the area where only UPD takes place and excludes the influence of OPD process. Therefore, the charge at the platform can be employed to estimate the quantity of UPD Cu and extract the number of active sites. And the number of active sites can be calculated with the equation:  $n=Q_{Cu}/2F$ , where Q is the UPD Cu stripping charge (Cu<sub>und</sub> $\rightarrow$ Cu<sup>2+</sup> +e<sup>-</sup>) and F is the Faraday constant.

The turnover frequency (TOF) calculation: The TOF (s<sup>-1</sup>) ca be calculated using the equation: TOF=I/(2Fn), where I (A) is the current during linear sweep voltammetry, F is the Faraday constant (C mol<sup>-1</sup>) and n is the number of active sites (mol). The formation of one hydrogen molecule require two electrons and thus the factor 1/2 is added into the equation.

**XAFS measurements and data processing:** The X-ray absorption fine structure data of Ru K-edge were collected at the BL14W1 station of the Shanghai Synchrotron Radiation Facility (SSRF). The storage ring was controlled at 3.5 GeV with a maximum current of 250 mA. The XAFS data of Ru foil was collected in transmission mode. The XAFS data of Ru-TA/ACC and Ru/ACC was collected at room temperature using a fixed-exit double-crystal Si (311) monochromator in fluorescence mode. The samples were cut into  $1 \times 1$  cm<sup>2</sup> square. The raw EXAFs data were processed using the ATHENA module achieved in the IFEFFIT software packages according to the standard procedures. The EXAFS contributions were separated from different coordination shells by using a hanning windows (dk=1.0 Å<sup>-1</sup>). Subsequently, the quantitative curve-fittings were carried out in the R-space with a Fourier transform k-space range of 3.0-11.6 Å<sup>-1</sup> using the module ARTEMIS of IFEFFIT. During the curve-fitting, the overall amplitude reduction factor S<sub>0</sub><sup>2</sup> was fixed to the best-fit value of 0.70 determined from fitting the data of metal Ru foil. For Ru-ACC and Ru-TA, fitting range

in R space are 1.0-3.0 Å and 1.0-2.0 Å.

## 1. Supplementary figures



Figure S1. Digital photo of TA powder and Ru-TA complex powder.



Figure S2. Raman spectra of Ru-TA coordination complex, TA and RuCl<sub>3</sub> powders.



Figure S3. Schematic route for the synthesis of Ru-TA/ACC.



Figure S4. (a), (b), (c) SEM images of the carbon cloth (CC); (d), (e), (f) SEM images of the activated carbon cloth (ACC); (g), (h) Nitrogen adsorption-desorption isotherms of the CC and ACC, respectively.



Figure S5. Ru-TA/ACC Ru-TA/ACC 15810. (a) Infrared spectra of ACC, Ru-TA/ACC and Ru-TA complex; (b) XPS spectra of Ru-TA/ACC.



Figure S6. HRTEM image of Ru-TA/ACC.



Figure S7. XRD patterns of Ru-TA/ACC and Ru/ACC.

The XRD patterns with no characteristic peaks of crystalline Ru indicates that the size of nanoparticles on Ru/ACC is small.



Figure S8. Aberration corrected HADDF-STEM atom image of Ru-TA/ACC.



Figure S9. (a), (b), (c) TEM images of Ru/ACC; (d) HRTEM image of Ru/ACC; (e) Elemental mapping analysis for the Ru/ACC.

Ru supported on the ACC (Ru/ACC) is also prepared by impregnation method and reduced by NaBH<sub>4</sub>. As observed on the TEM images, the lattice spacing of the nanoparticles is determined to be 0.205 nm which is consistent with the (101) facet of the metal Ru crystal (JCPDS: 65-7645). Inhomogeneous distribution of Ru nanoparticles on the ACC is further corroborated by the HADDF-STEM imaging combined with element mapping analysis.



Figure S10. The experimental Fourier transform EXAFS spectra and best-fitting curves of Ru/ACC, Ru-TA/ACC. Fitting range:1.0 Å-3.0 Å (Ru/ACC), 1.0 Å-2.0 Å (Ru-TA/ACC).



Figure S11. (a) High-resolution XPS spectra of Ru 3p for Ru-TA/ACC and Ru/ACC; (b) High-resolution XPS spectra of Ru 3d and C 1s for Ru-TA/ACC and Ru/ACC. In Ru 3p spectrum of Ru-TA/ACC, there are two major peaks located at 486.3 eV and 463.9 eV, assigned to the typical Ru  $3p_{1/2}$  and  $3p_{3/2}$  core levels of Ru<sup>3+</sup>, respectively. In Ru 3d spectrum, the peak located at 281.98 eV corresponds with Ru<sup>3+</sup> as well. In Ru 3p spectra for Ru/ACC, Ru<sup>0</sup> yields peaks at 484.3 and 462.3 eV corresponding to Ru  $3p_{1/2}$  and  $3p_{3/2}$ , respectively. The spin-orbit splitting is found to be 22 eV, which

is consistent well with the one expected for Ru<sup>0</sup>-containing composites. The rest of the peaks in Ru 3p are assigned to Ru<sup>n+</sup>.



Figure S12. Mass activity of Ru-TA/ACC and Pt/C (20 wt%) in 1.0 M KOH.



Figure S13. (a) The cyclic voltammetry scans for the Ru-TA/ACC in different solutions; (b) The LSV curves for the stripping of Cu deposited at different overpotentials from 0.175 to 0.265 V in a 0.5 M  $H_2SO_4 + 20$  mM CuSO<sub>4</sub> + 60 mM NaCl solution on Ru-TA/ACC; (c) The current-voltage scan for the Ru/ACC in different solutions; (d) The LSV curves for the stripping of Cu deposited at different overpotentials from 0.175 to 0.265 V in a 0.5 M  $H_2SO_4 + 20$  mM CuSO<sub>4</sub> + 60 mM NaCl solution on Ru-TA/ACC; (c) The current-voltage scan for the Ru/ACC in different solutions; (d) The LSV curves for the stripping of Cu deposited at different overpotentials from 0.175 to 0.265 V in a 0.5 M  $H_2SO_4 + 20$  mM CuSO<sub>4</sub> + 60 mM NaCl solution on Ru/ACC.

The number of active sites in electrocatalysts was then evaluated by the underpotential deposition (UPD) of copper on Ru. The Cu UPD method is based on the principle that the active sites for the reduction of protons are also effective for the reduction of  $Cu^{2+}$  ions at an underpotential condition. Therefore, the charge required for oxidative stripping of copper produced during UPD process can be employed to estimate the number of active sites. As shown in Figure S13a, no oxidation or reduction peaks appear in the cyclic voltammetry (CV) in 0.5 M H<sub>2</sub>SO<sub>4</sub>. When CV scans was collected in the typical solution of UPD method (0.5 M H<sub>2</sub>SO<sub>4</sub> + 20 mM CuSO<sub>4</sub>), one reduction and one oxidation peak are found, indicating the overlap of UPD and overpotential deposition (OPD) process. Cl<sup>-</sup> ion is an ideal additive to resolve the UPD and OPD peaks because it can absorb on the UPD adlayer instantly and thus inhibit the OPD process. Therefore, in a 0.5 M H<sub>2</sub>SO<sub>4</sub> + 20 mM CuSO<sub>4</sub> + 60 mM NaCl solution, peaks of UPD, OPD and the corresponding stripping are distinct in CV curves. Then, LSV was performed at an initial overpotential from 0.175 to 0.265 V to strip Cu.



Figure S14. (a) and (b) Cyclic voltammetry curves of Ru-TA/ACC and Ru/ACC, respectively, the arrows represent the increased scan rate from 5 mV/s to 10 mV/s.



Figure S15. (a) The current-voltage scan in a 0.5 M  $H_2SO_4 + 20$  mM  $CuSO_4 + 60$  mM NaCl solution, (b) The LSV curves for the stripping of Cu deposited at different overpotentials from 0.175 to 0.265 V in a 0.5 M  $H_2SO_4 + 20$  mM  $CuSO_4 + 60$  mM NaCl solution, (c) The charges required to strip the Cu deposited at different underpotentials for the Ru-TA/ACC after constant electrolysis for 130 h; (d) The current-voltage scan in a 0.5 M  $H_2SO_4 + 20$  mM  $CuSO_4 + 60$  mM NaCl solution, (e) The LSV curves for the stripping of Cu deposited at different overpotentials from 0.175 to 0.265 V in a 0.5 M  $H_2SO_4 + 20$  mM  $CuSO_4 + 60$  mM NaCl solution, (e) The LSV curves for the stripping of Cu deposited at different overpotentials from 0.175 to 0.265 V in a 0.5 M  $H_2SO_4 + 20$  mM  $CuSO_4 + 60$  mM NaCl solution, (f) The charges required to strip the Cu deposited at different underpotentials for the Ru/ACC after constant electrolysis for 30 h.



Figure S16. Aberration corrected HADDF-STEM and HRTEM atom image of Ru-TA/ACC after continuous electrolysis for 130 h.



Figure S17. (a), (b), (c) TEM images of Ru/ACC after constant electrolysis for 30 h; (d) High-resolution TEM image of Ru/ACC after constant electrolysis for 30 h.



Figure S18. High-resolution XPS spectra of Ru 3p for Ru-TA/ACC after continuous electrolysis for 130 h.



Figure S19. (a) Potential-time curves of Ru-TA/ACC after calculated at 300 °C for 1 h in nitrogen; (b) Corresponding polarization curves of Ru-TA/ACC, Ru-TA/ACC after calculated at 300 °C for 1 h in nitrogen before and after constant electrolysis for

15 h;



Figure S20. Polarization curves for Ru-TA/ACC, Ru/ACC and 20 wt% commercial Pt/C in 1.0 M PBS (a) and 0.5 M H<sub>2</sub>SO<sub>4</sub> (b).



Figure S21. Polarization curves for Ru-TA/ACC at different temperatures in 1.0 M KOH.

The development of HER catalysts that function well under high and low temperatures is of great significant for water electrolysis devices used at high latitudes and in hilly regions, respectively. Figure S19 indicates that Ru-TA/ACC exhibits comparable performance between at low temperature of 0 °C and room temperature of 20 °C. With temperature increase, the activity gradually enhanced and reach the optimal at 60 °C with an extremely low overpotential of 25 mV at 10 mA cm<sup>2</sup>. These results indicate that Ru-TA/ACC can be employed as an efficient HER catalyst under a wide temperature range.

## 2. Supplementary tables

Sample	shell	Ν	R (Å)	$\Delta E_0 (eV)$	σ²(10 <sup>-3</sup> Ų)	R-factor
Ru/ACC	Ru-O	$4.8 \pm 1.0$	$1.99\pm0.02$	$7.8\pm2.4$	$7.6\pm3.1$	0.019
	Ru-Ru	$\textbf{3.4} \pm \textbf{1.5}$	$2.67\pm0.02$	$5.6\pm2.9$	$9.7\pm3.7$	
Ru-TA/ACC	Ru-O1	$\textbf{2.1} \pm \textbf{1.3}$	$1.83\pm0.07$	$3.5\pm 5.0$	3.0	0.007
	Ru-O2	$\textbf{6.4} \pm \textbf{1.5}$	$2.01\pm0.04$	$3.5\pm5.0$	3.0	

Table S1. Ru K-edge fitting parameters

N, coordination numbers; R, the internal atomic distance;  $\sigma^2$ , Debye-Waller factor;  $\Delta E_0$ , the edge-energy shift.

	( )	
Vibration type	TA	Ru-TA
υ <sub>O-H</sub>	3388 s	3437 s
υ <sub>C=O</sub>	1718 s	1693 s
υ <sub>C=C</sub> (Ph)	1616 s	1577 s
υ <sub>C=C</sub> (Ph)	1534 m	1504 m
υ <sub>C=C</sub> (Ph)	1446 m	w
υ <sub>C-O</sub> (ester)	1321 s	1366 s
υ <sub>C-O</sub>	1198 s	1199 s
υ <sub>C-C</sub>	1084 m	1113 w
$\beta_{=CH}$	1026 s	1046 s
$\delta_{\text{C-H}}$ (Ph)	868 w	926 w
$\delta_{\text{C-H}}$ (Ph)	591 w	w

Table S2. Infrared spectra data of tannic acid and ruthenium-tanic acid complex

(KBr, cm<sup>-1</sup>).

Table S3. Comparison of the electrocatalytic HER performance of the Ru-TA/ACC with the recently reported electrocatalysts.

Catalysts	Ŋ-jª	Electrolyte	References
	29-10	1.0 M KOH	
Ru-TA/ACC	60-10	1.0 M PBS	This work
	112-10	0.5 M H <sub>2</sub> SO <sub>4</sub>	
	32-10	1.0 M KOH	
Ru@CN	100-10	1.0 M PBS	Energy Environ. Sci. 2018, 11, 800
	126-10	0.5 M H <sub>2</sub> SO <sub>4</sub>	
Ru@C₂N	17-10	1.0 M KOH	Nat. Nanotech. 2017, 12, 441
CoMoS <sub>x</sub>	158-5	0.1 M KOH	Nature Mater. 2016, 15, 197
RuCo alloy	28-10	1.0 M KOH	Nat. Commun. 2017, 8 ,14969
Ru/CQDs	47-10	1.0 M KOH	Adv. Mater. 2018, 30, 1800676
RuP <sub>2</sub> @NPC	52-10	1.0 M KOH	Angew. Chem. 2017, 56, 11559
MoN-	154-10	1.0 M KOH	Adv. Mater. 2018, 30, 1704156
Mo <sub>2</sub> C/HGr			
R-TiO <sub>2</sub> : Ru	150-10	0.1 M KOH	J. Am. Chem. Soc. 2018, 140, 5719
Ru/C <sub>3</sub> N <sub>4</sub> /C	79-10	0.1 M KOH	J. Am. Chem. Soc. 2016, 138, 16174
MoC <sub>x</sub>	140-10	0.5 M H <sub>2</sub> SO <sub>4</sub>	Nat. Commun. 2015, 6, 6512
Cu <sub>3</sub> P	143-10	0.5 M H <sub>2</sub> SO <sub>4</sub>	Angew. Chem. 2014, 53, 9577
nanowires			
Fe-doped	78-10	0.5 M H <sub>2</sub> SO <sub>4</sub>	Adv. Mater. 2017, 29, 1602441
CoP/Ti			
CoP@BCN	87-10	0.5 M H <sub>2</sub> SO <sub>4</sub>	Adv. Energy Mater. 2017, 7, 1601671
Co-NRCNTs	260-10	0.5 M H <sub>2</sub> SO <sub>4</sub>	Angew. Chem. 2014, 126, 4461

[a]  $\eta$  represents the overpotential calculated at the current density of j (mA cm<sup>2</sup>).

Catalysts	Mass content (%)	Area content (ug/cm <sup>2</sup> )
Ru-TA/ACC	0.058	10.1
Ru/ACC	0.110	18.6
Ru-TA/ACC after constant electrolysis for 130 h	0.057	9.9
Ru/ACC after constant elctrolysisi for 30 h	0.061	10.3

Table S4. Ru content of the catalysts determined by ICP-AES analysis.