Electronic Supplementary Information (ESI)

Biomimetic Organization of Ruthenium-doped Collagen-based Carbon Scaffold for Hydrogen Evolution

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1. Materials

All chemicals were used as received without further purification. Ruthenium(III) chloride ($RuCl_3$, Ru content 45-55%), sodium tripolyphosphate (TPP, Mw 367.9) and phosphate buffered saline (PBS) were purchased from Sigma-Aldrich.(add all chemicals). Rat tail tropocollagen was purchased from Corning® (4.62 mg/mL, pH <2).

2. Calculation of Turnover Frequency (TOF)

The TOF value (s^{-1}) was calculated from equation (1):

$$TOF = \frac{J * A}{2 * F * n} \quad (1)$$

J is normalized by geometric area of GCE (0.07065 cm^2), A is the geometric area of GCE (0.07065 cm^2), F is the Faraday constant, n is the mole number of active sites on the electrode, n is the mole number of active sites for HER, via equation below:

$$n = \frac{m_{loading} * A * r}{M_w} \quad (2)$$

where $m_{loading}$ is the loading mass via drop-casting, A is the geometric area of GCE (0.07065 cm^2), r is the weight ratio of active metal in catalyst, M_w is the molecular weight of active sites.

3. Supplementary Figures

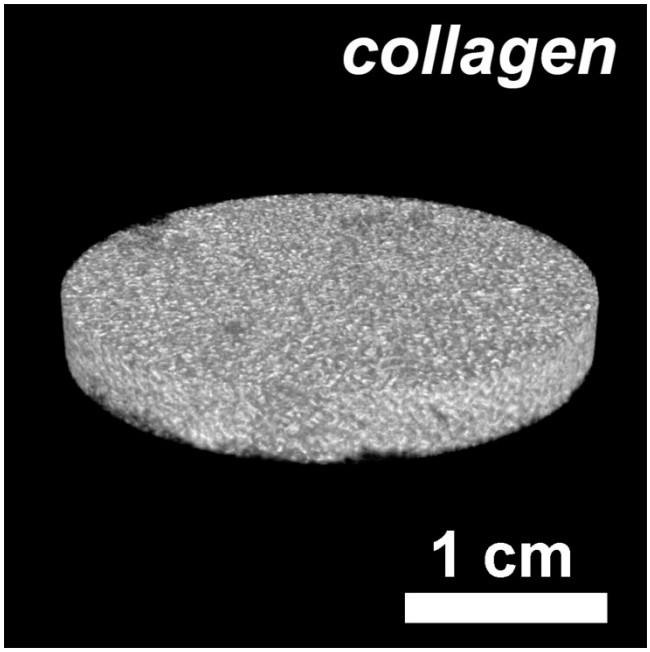


Fig. S1. Representative micro-CT image of a pure collagen scaffold.

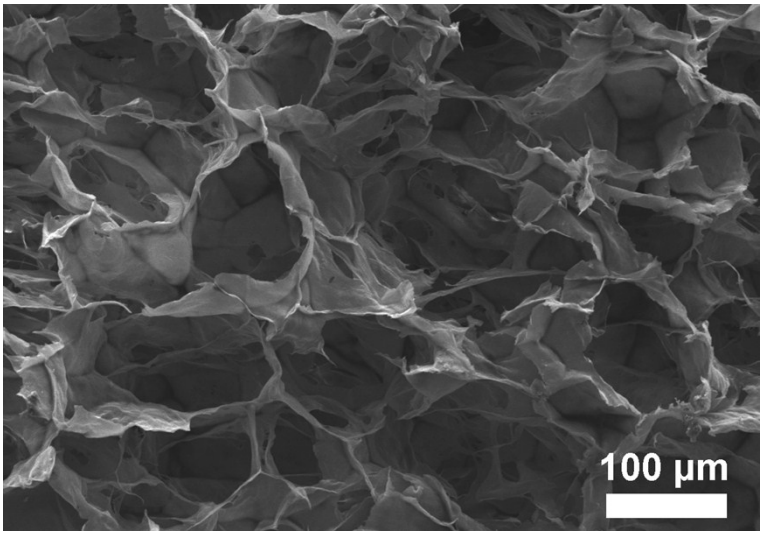


Fig. S2. Representative SEM image of 3D collagen scaffold with an average pore diameter of 136.74 ± 39.34 µm.

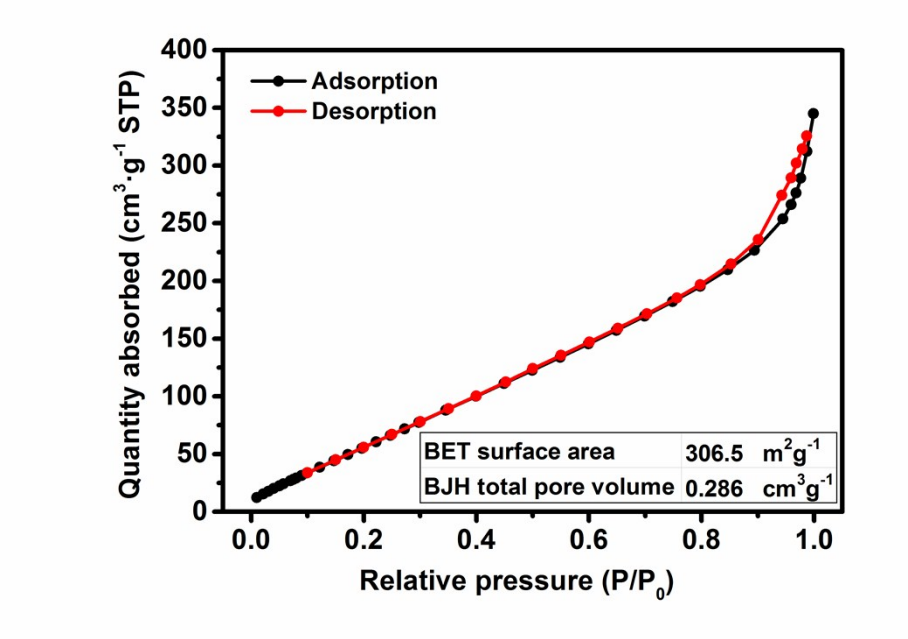


Fig. S3. N_2 adsorption/desorption isotherms of Ru-CCS.

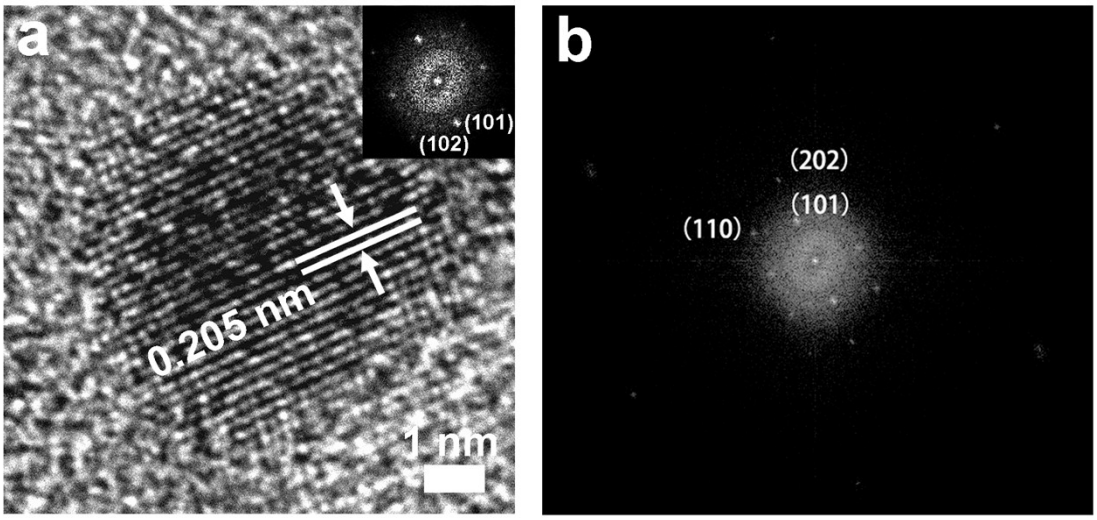


Fig. S4. (a) High-magnification TEM image of Ru-CCS showing the (101) lattice fringes of the hexagonal Ru nanoparticle. Inset: SAED image of Ru-CCS. (b) Fast Fourier transform (FFT) spot pattern of Ru nanoparticles in Ru-CCS.

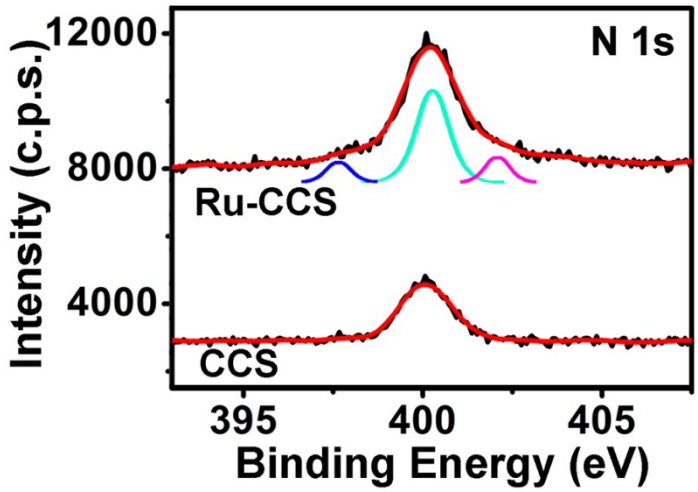


Fig. S5. High-resolution XPS spectra of N1s of Ru-CCS catalyst.

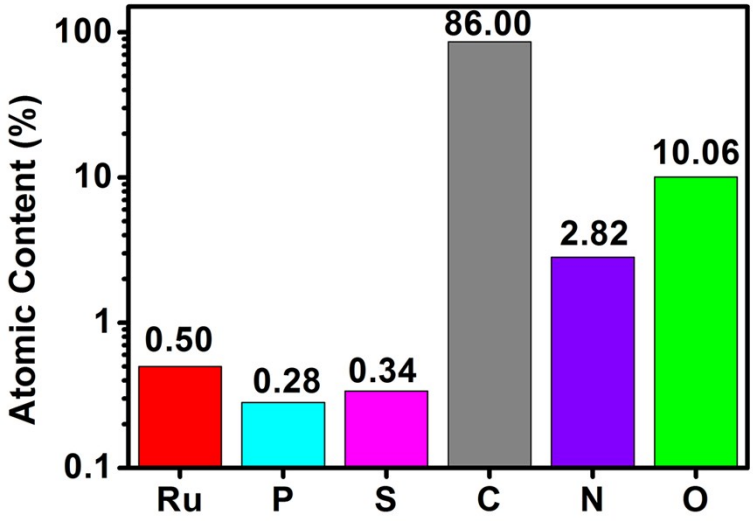


Fig. S6. Atomic contents percent of ruthenium, phosphorus, sulfur, carbon, nitrogen and oxygen in Ru-CCS measured by EDX-mappings.

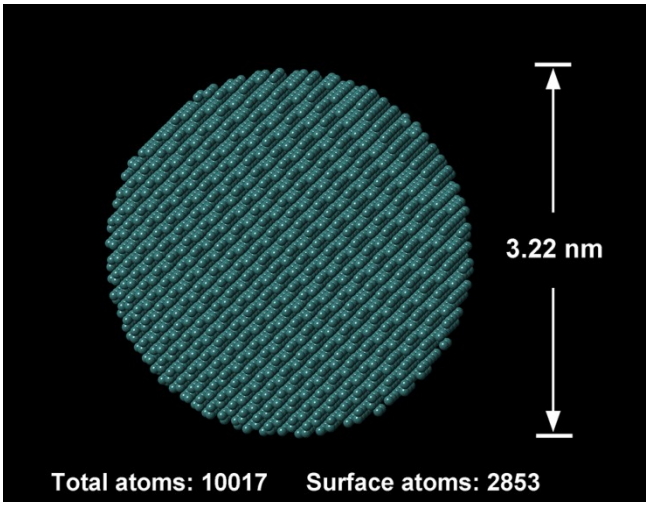


Fig. S7. Schematic representation of Ru nanoparticles in Ru-CCS. The Ru nanoparticle, with diameter of 3.22 nm, has 10017 atoms and 2853 atoms located at surface.

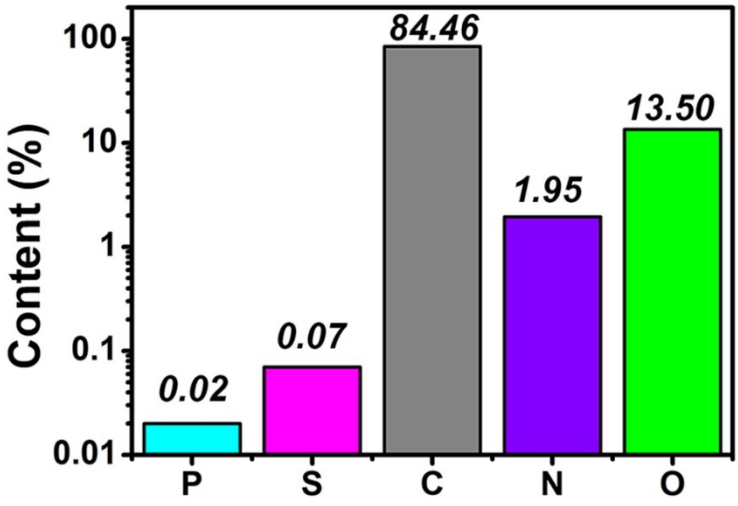


Fig. S8. Atomic content percent of phosphorus, sulfur, carbon, nitrogen and oxygen in pure CCS measured by inductively coupled plasma optical emission spectrometry (ICP-OES).

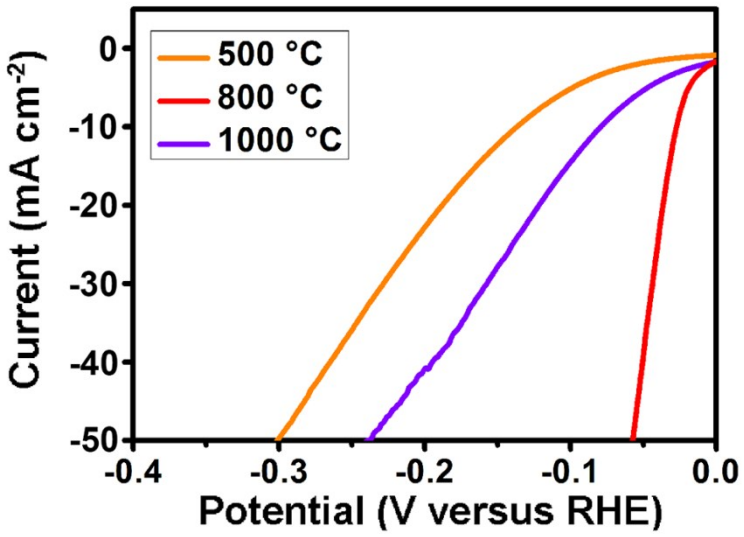


Fig. S9. Linear sweep voltammograms curves of Ru-CCS annealed at 500°C, 800°C and 1000°C, respectively.

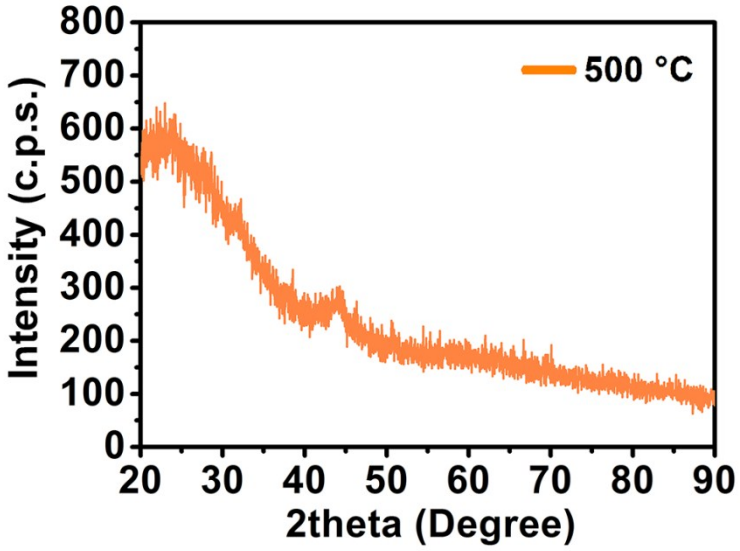


Fig. S10. The XRD pattern of Ru-CCS annealed at 500°C. Lower annealing temperature is not conducive to crystallization of Ru.

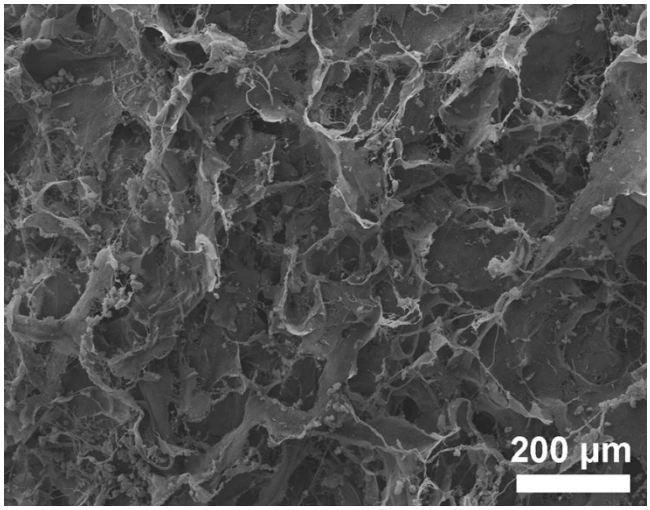


Fig. S11. Representative SEM image of Ru-CCS annealed at 1000°C. Higher temperature leads to disintegration of 3D porous structure and aggregation of Ru nanoparticles.

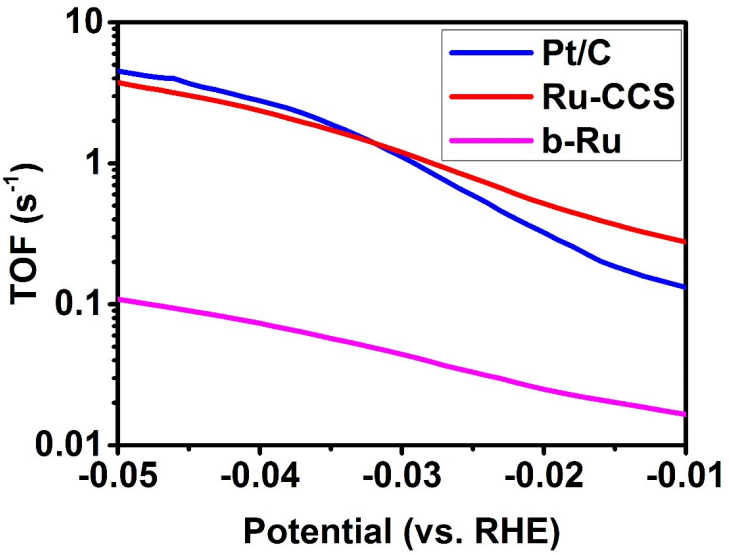
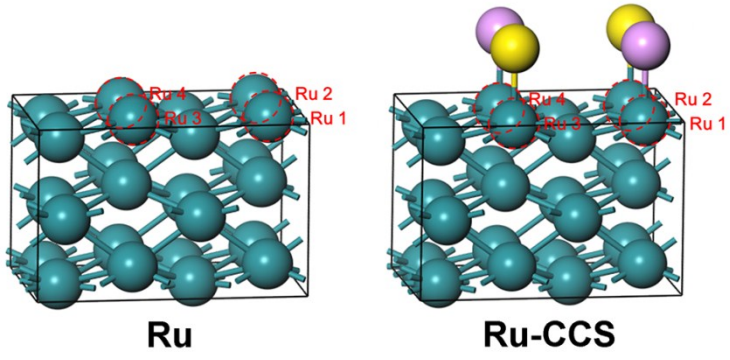


Fig. S12 The relationship between TOF values and the measured potentials for the Ru-CCS, Pt/C and bulk-Ru electrocatalysts.



	Ru 1	Ru 2	Ru 3	Ru 4	Average
Ru	-0.05 e⁻	-0.05 e⁻	-0.05 e⁻	-0.05 e⁻	-0.05 e⁻
Ru-CCS	-0.38 e⁻	-0.24 e⁻	-0.24 e⁻	-0.38 e⁻	-0.31 e⁻

Fig. S13. Localized electrons in Ru and Ru-CCS.

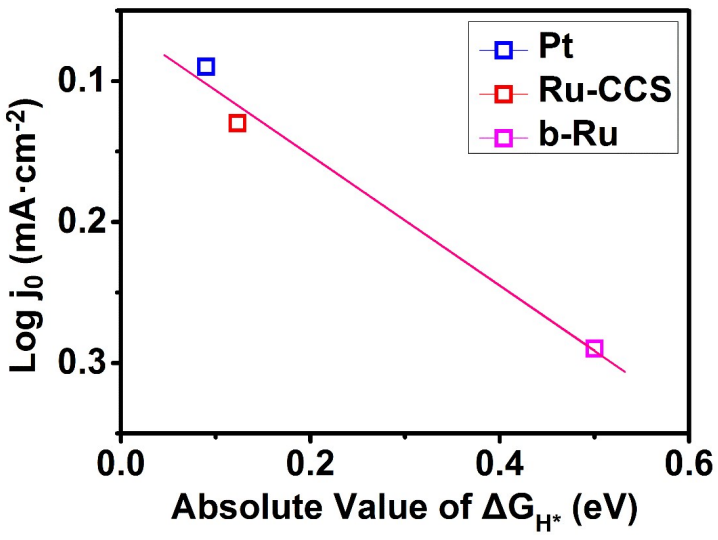


Fig. S14 Relationship between calculated $\triangle G_{H^*}$ and measured j_0 value.