

Electronic Supplementary Information for

P-modified hollow carbon mesoporous nanospheres decorated with
ultrafine OsP alloy nanoparticles for nonacidic hydrogen evolution

Min Liu,^{a,b} Keke Shi,^a Zhongyao Duan,^a Mei Zhang,^a You Xu,^a Ziqiang Wang,^a Xiaonian Li,^a

*Liang Wang^a and Hongjing Wang^{*a}*

^a State Key Laboratory Breeding Base of Green-Chemical Synthesis Technology, College of Chemical Engineering, Zhejiang University of Technology, Hangzhou 310014, P. R. China.

^b Inner Mongolia Key Laboratory of Environmental Chemistry, College of Chemistry and Environmental Science, Inner Mongolia Normal University, Hohhot, Inner Mongolia 010022, P. R. China.

Corresponding author

*E-mail: hjw@zjut.edu.cn

Experimental section

Materials and Chemicals.

Tetraethyl orthosilicate Tetrapropyl (TEOS), orthosilicate (TPOS), ammonium hydroxide (28-30%), resorcinol (99%), formaldehyde (37 wt% in H₂O), hydrofluoric acid (40-45%), potassium hexachloroosmate(IV) (K₂OsCl₆), and sodium hypophosphite (NaH₂PO₂) were purchased from Aladdin. Nafion 117 solution (5 wt%), and commercial Pt/C catalysts were obtained from Sigma-Aldrich.

Synthesis of samples

The SiO₂@SiO₂/RF nanospheres were prepared according to previous literature.^{1,2} Typically, 70 ml of ethanol, 10 ml of deionized water and 3.0 mL of ammonium hydroxide, 1.75 mL of TPOS, and 1.75 mL of TEOS were stirred together at room temperature for 15 minutes. After the reaction, resorcinol (0.4 g) and 0.56 mL of formaldehyde (37 wt%) were added to the above solution. And continuing stirring at room temperature for 24 h, the SiO₂@SiO₂/RF nanospheres were collected by centrifugation, washed several times with ethanol, and then dried overnight under vacuum at 60°C. Then, 25 mg of SiO₂@SiO₂/RF nanospheres were dispersed into 30 ml of ethanol under magnetic stirring and heated at 50 °C. Under magnetic stirring at 350 rpm, 30 mg of K₂OsCl₆ and 0.3 g NaH₂PO₂ were successively added to the above mixture, and the color of the solution was found to change to brownish-black. This step was carried out overnight and the solid was collected by centrifugation and dried under vacuum.

The SiO₂@SiO₂/OsP-RF nanospheres were placed in a tube furnace and heated at controlled temperatures (500, 600, 700, and 800 °C) for 2 h at a heating rate of 5 °C min⁻¹. SiO₂@SiO₂/OsP-RF nanospheres were always kept under nitrogen for pyrolysis and subsequently collected by centrifugation after removal of the SiO₂ template with a 20 wt% HF solution. Samples were denoted as OsP/PHMCSs-T where T was 500, 600, 700, or 800. The Os/HMCSs-600 counterpart was synthesized with similar procedure without the addition of NaH₂PO₂ and the PHMCSs-600 counterpart was synthesized with similar procedure without the addition of K₂OsCl₆.

Characterization

Scanning electron microscope (SEM) images were obtained on a Zeiss Gemini 500 microscope at 10 kV. Transmission electron microscopy (TEM), high-resolution TEM (HR-TEM), high angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), and energy-

dispersive X-ray spectroscopy (EDX) images were obtained on a TalosS-FEG microscope at 200 kV. Powder X-ray diffraction (XRD) patterns were obtained using a panalytic X'Pert-PRO X-ray diffractometer under Cu-K α ($\lambda = 0.1542$ nm) radiation. X-ray photoelectron spectroscopy (XPS) analysis was carried out on an Axis Ultra spectrometer (Kratos Analytical) using a monochromatic Al K α X-ray source (1486.7 eV) with an operating voltage of 15 kV.

Electrochemical measurements

Electrocatalytic measurements were carried out in the CHI 760E electrochemical workstation with a standard three-electrode system. Catalyst-decorated glassy carbon electrode (GCE, 3 mm diameter), Hg/HgO or Ag/AgCl, and graphite rod were used as working, reference, and counter electrodes respectively. The catalyst suspension was prepared by dispersing 1.0 mg of catalyst in a 200 μ L solution containing 190 μ L of isopropanol and 10 μ L of a 5 wt% Nafion solution, followed by sonication for 5 min. The catalyst suspension was then pipetted onto the GCE surface using a micropipette. Working electrodes were prepared by placing 5 μ L drops of catalyst ink on the polished GCE surface and drying in an oven at 50°C. For all electrochemical measurements, an aqueous solution of 1.0 M KOH and 1.0 M PBS (pH = 7.0) were used as the electrolyte. The polarization curve of the HER was tested by linear sweep voltammetry (LSV) with a scan rate of 5 mV s⁻¹. For the iR correction (95%), the uncompensated ohmic resistance of the electrode in the electrolyte solution was measured by Electrochemical Impedance Spectroscopy (EIS) before the electrochemical test of the electrode. The accelerated degradation test (ADT) was conducted within the potential range of 0-0.1 V (vs. RHE) at a scan rate of 100 mV s⁻¹. The catalytic durability of OsP/PHMCSs-600 is further confirmed by chronopotentiometric (V-t) test at a constant current density of 10 mA cm⁻². Moreover, a catalyst-decorated glassy carbon electrode is subjected to V-t test for 28 h and 100 h. All potentials in this work were calibrated to the reversible hydrogen electrode (RHE) scale.

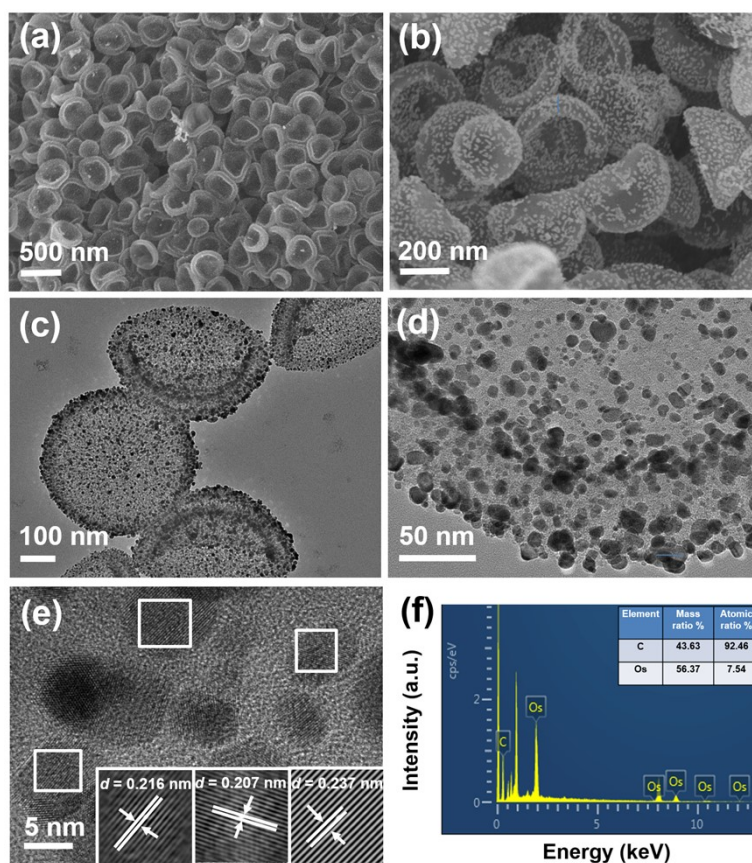


Fig. S1 (a, b) SEM images, (c, d) TEM images, (e) HRTEM image, (f) EDX spectrum of Os/HMCSs-600. The inset in (e) displays the corresponding Fourier-filtered lattice fringes.

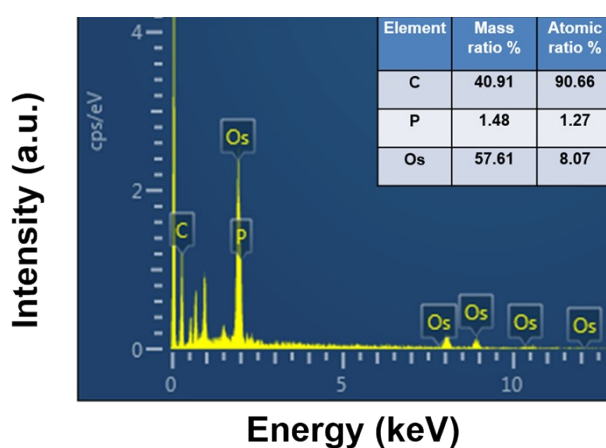


Fig. S2 EDX spectrum of the OsP/PHMCSs-600.

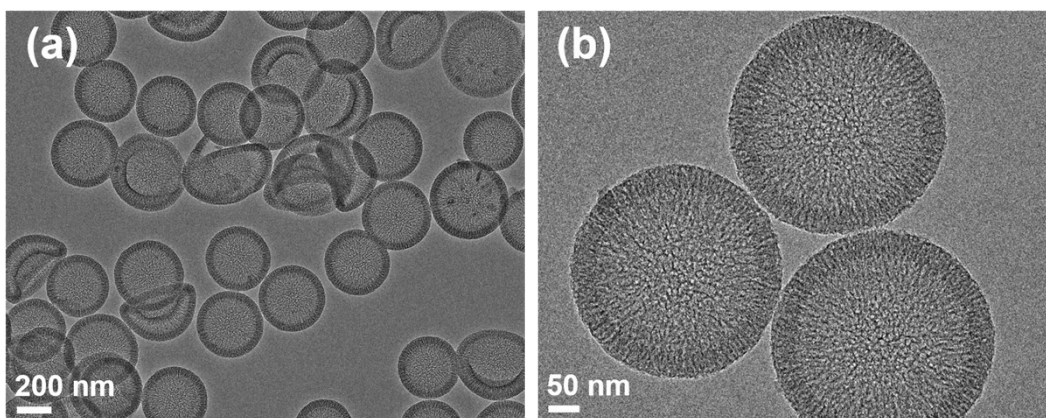


Fig. S3 TEM images of (a, b) HMCSs-600.

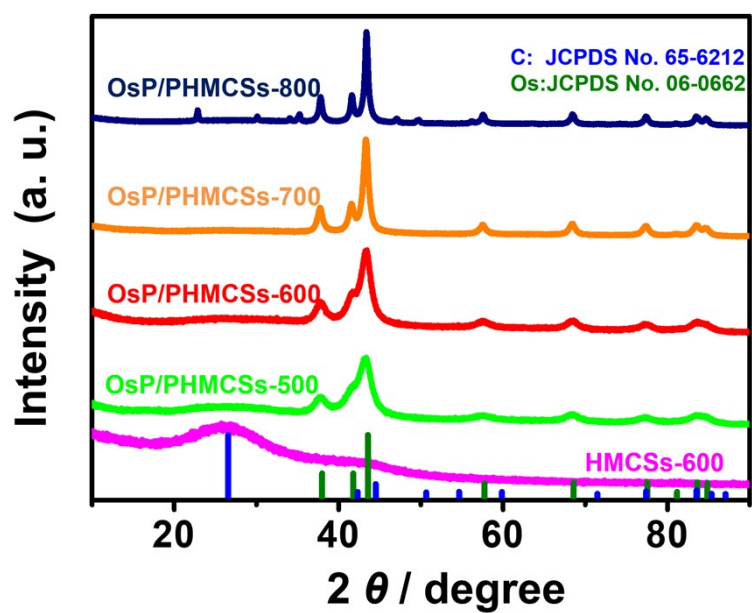


Fig. S4 XRD patterns of various catalysts.

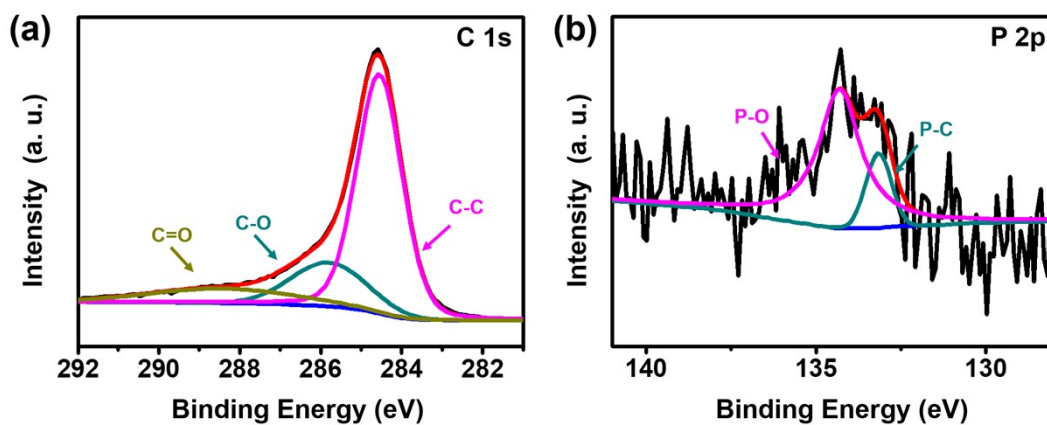


Fig. S5 XPS spectra of the C 1s (a) and P 2p (b) for the PHMCSs-600.

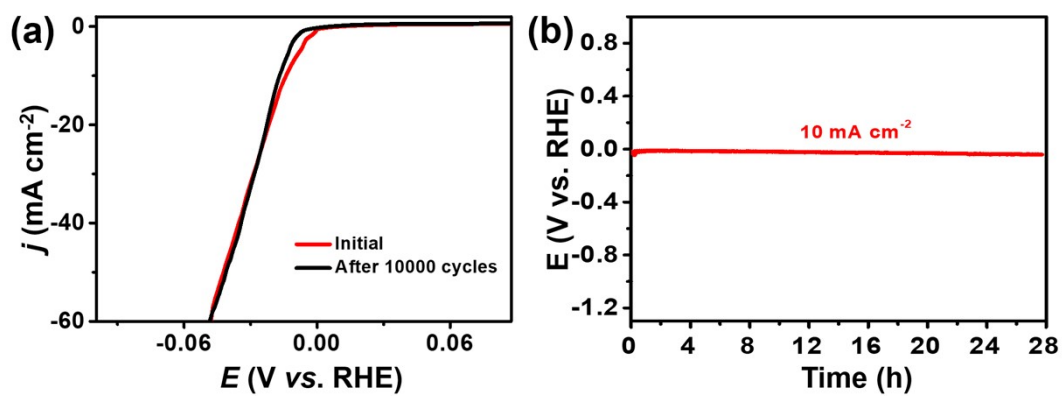


Fig. S6 (a) HER polarization curves (with iR correction) for OsP/PHMCSs-600 before and after 10000 CVs cycling tests. (b) The V-t curve of OsP/PHMCSs-600 with a constant cathode-current density of 10 mA·cm⁻² for 28 h in 1.0 M KOH.

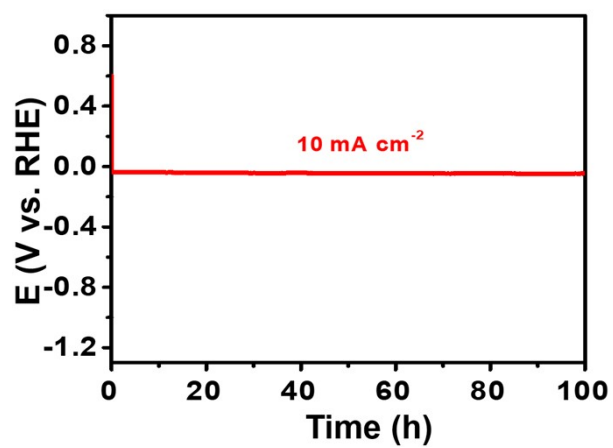


Fig. S7 The V-t curve of OsP/PHMCSs-600 with a constant cathode-current density of 10 mA·cm⁻² for 100 h in 1.0 M KOH.

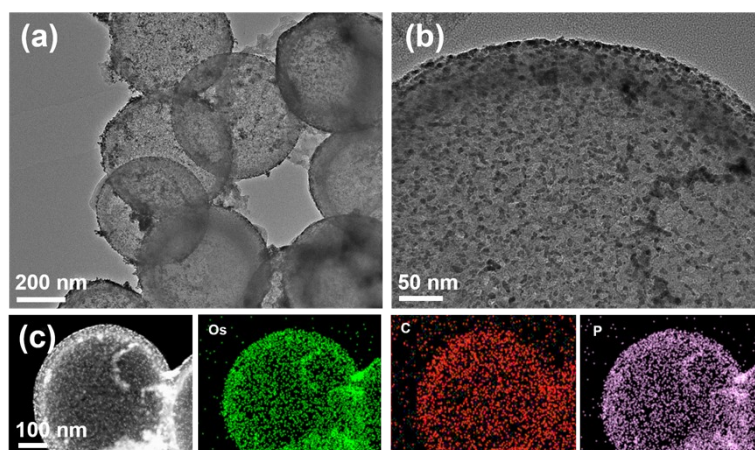


Fig. S8 (a, b) TEM and (c) HAADF-STEM and elemental mapping images of the OsP/PHMCSs-600 after catalytic stability testing.

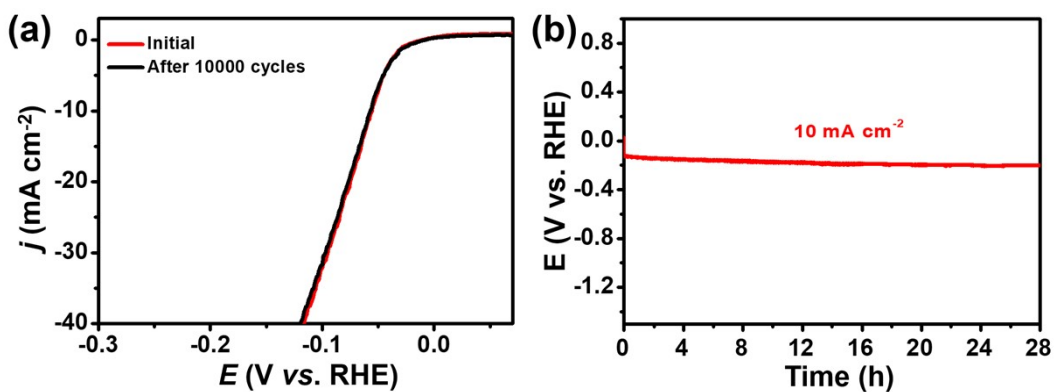


Fig. S9 (a) HER polarization curves (with iR correction) for OsP/PHMCSs-600 before and after 10000 CVs cycling tests. (b) The V-t curve of OsP/PHMCSs-600 with a constant cathode-current density of $10 \text{ mA} \cdot \text{cm}^{-2}$ for 28 h in 1.0 M PBS.

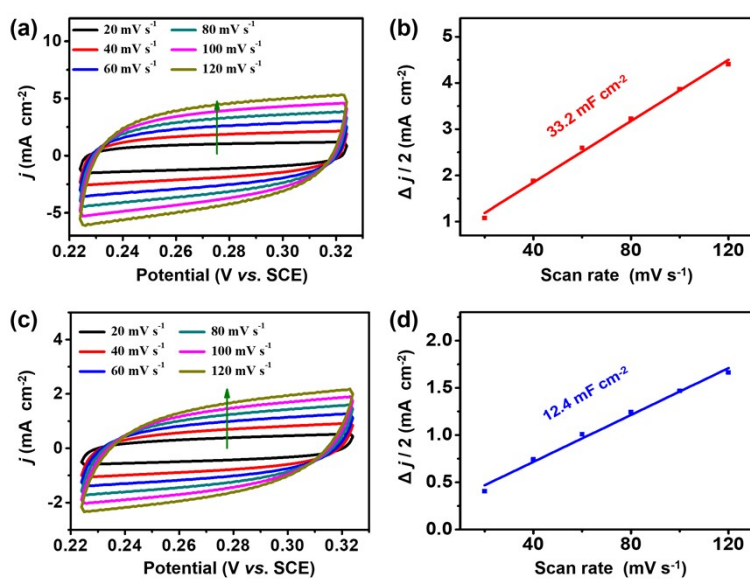


Fig. S10 (a, c) Typical cyclic voltammogram (CV) curves of OsP/PHMCSs-600 and Os/HMCSs-600 with different scan rates. (b, d) Capacitive current densities at 0.274 V (vs. RHE) derived from CVs against scan rates for the samples in 1.0 M KOH.

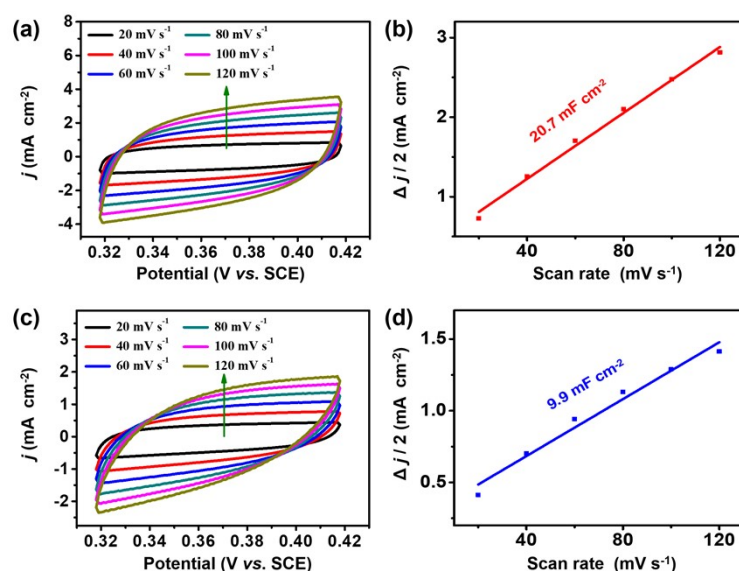


Fig. S11 (a, c) Typical cyclic voltammogram (CV) curves of OsP/PHMCSs-600 and Os/HMCSs-600 with different scan rates. (b, d) Capacitive current densities at 0.368 V (vs. RHE) derived from CVs against scan rates for the samples in 1.0 M PBS.

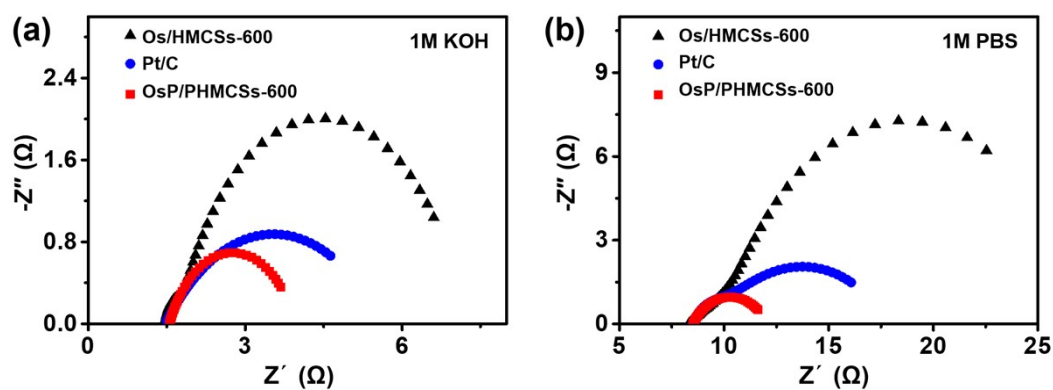


Fig. S12 Nyquist plots of various catalysts in the different electrolytes under applied potentials of (a) -0.05 V and (b) -0.37 V (vs. RHE).

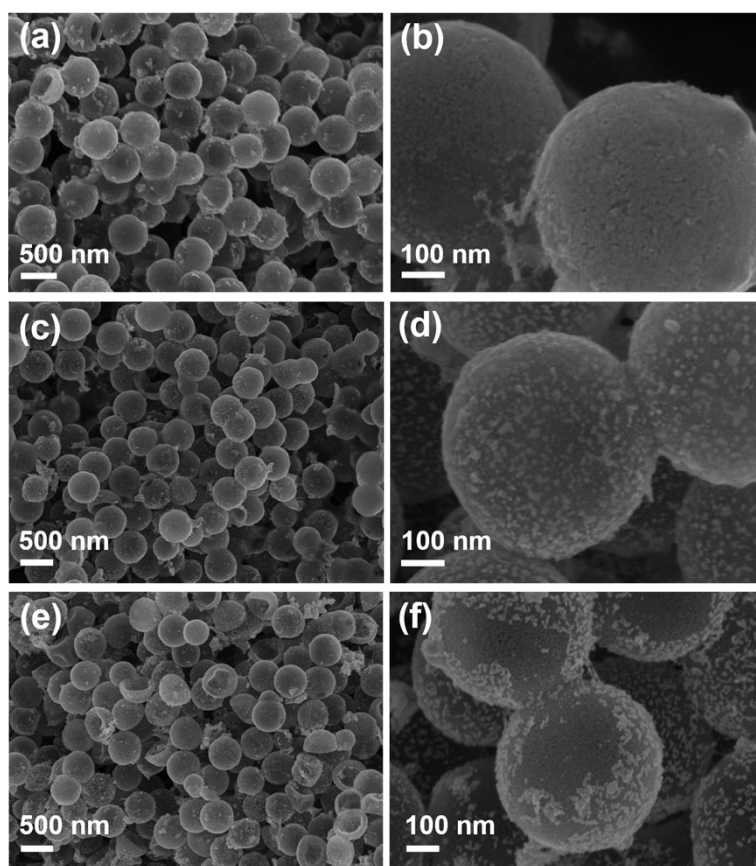


Fig. S13 SEM images of (a, b) OsP/PHMCSs-500, (c, d) OsP/PHMCSs-700, and (e, f) OsP/PHMCSs-800.

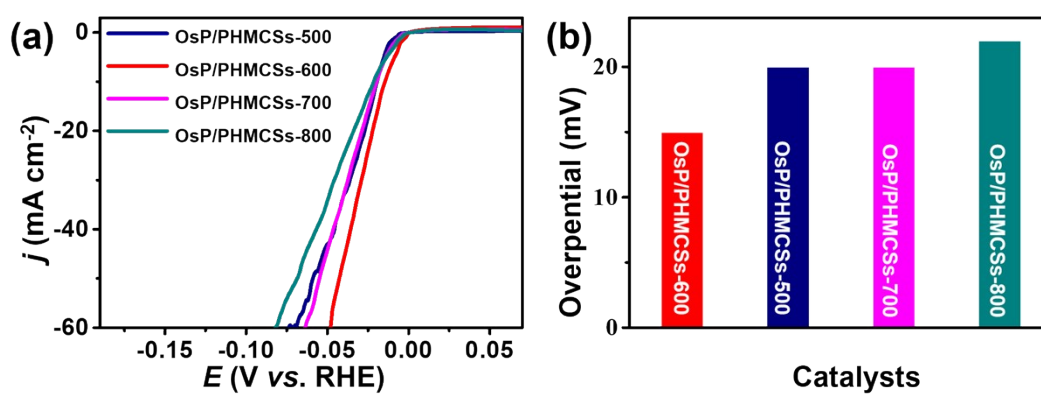


Fig. S14 (a) LSV curves (with iR correction) for various electrodes collected in 1.0 M KOH. (b) Comparison of the overpotentials at 10 mA cm^{-2} .

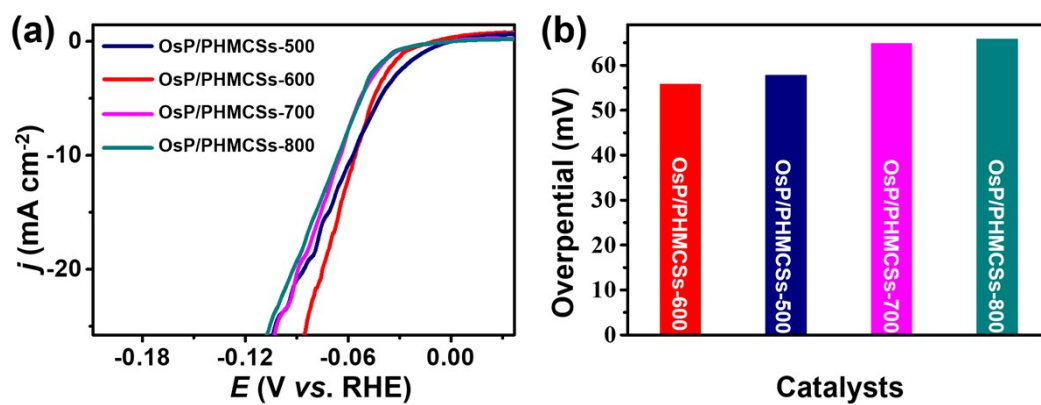


Fig. S15 (a) LSV curves (with iR correction) for various electrodes collected in 1.0 M PBS. (b) Comparison of the overpotentials at 10 mA cm⁻².

Table S1. Comparisons of the HER activity for the OsP/PHMCSs-600 and some recently reported catalysts under alkaline conditions.

Catalysts	Electrolyte	Current density	η_{10} (mV)	Ref.
OsP/PHMCSs-600	1.0 M KOH	10 mA cm⁻²	15	This work
OsP ₂ @NPC	1.0 M KOH	10 mA cm ⁻²	90	3
OsP ₂ @NPC	1.0 M KOH	10 mA cm ⁻²	70	4
Au–Rh aerogel	1.0 M KOH	10 mA cm ⁻²	22	5
RuCo@NC-600	1.0 M KOH	10 mA cm ⁻²	34	6
RhCoB aerogels	1.0 M KOH	10 mA cm ⁻²	43.6	7
Rh ₂ S ₃ /NC	1.0 M KOH	10 mA cm ⁻²	38	8
Ru@WNO-C	1.0 M KOH	10 mA cm ⁻²	24	9
Ni@Ni ₂ P–Ru HNRs	1.0 M KOH	10 mA cm ⁻²	51	10
Au–Ru NWs	1.0 M KOH	10 mA cm ⁻²	50	11
Rh ₂ P/NPC	1.0 M KOH	10 mA cm ⁻²	17	12

Table S2. Comparisons of the HER activity for the OsP/PHMCSs-600 and some recently reported catalysts under neutral conditions.

Catalysts	Electrolyte	Current density	η_{10} (mV)	Ref.
OsP/PHMCSs-600	1.0 M PBS	10 mA cm⁻²	56	This work
OsP ₂ @NPC	1.0 M PBS	10 mA cm ⁻²	144	3
RuCo@NC-600	1.0 M PBS	10 mA cm ⁻²	60	6
RhCoB aerogels	1.0 M PBS	10 mA cm ⁻²	113	7
Ru-S-Sb	1.0 M PBS	10 mA cm ⁻²	153	13
1D-RuO ₂ -CN _x	1.0 M PBS	10 mA cm ⁻²	356	14

References

1. X.-K. Wan, H. B. Wu, B. Y. Guan, D. Luan and X. W. Lou, *Adv. Mater.*, 2020, **32**, 1901349.
2. Z. Li, J. Zhang, B. Y. Guan and X. W. Lou, *Angew. Chem., Int. Ed.*, 2017, **56**, 16003-16007.
3. S. Chakrabartty, B. K. Barman and C. R. Raj, *Chem. Commun.*, 2019, **55**, 4399-4402.
4. L. Fang, Y. Wang, X. Yang, H. Zhang and Y. Wang, *J. Catal.*, 2019, **370**, 404-411.
5. R. Du, W. Jin, R. Hübner, L. Zhou, Y. Hu and A. Eychmüller, *Adv. Energy Mater.*, 2020, **10**, 1903857.
6. F. Zhang, Y. Zhu, Y. Chen, Y. Lu, Q. Lin, L. Zhang, S. Tao, X. Zhang and H. Wang, *J. Mater. Chem. A*, 2020, **8**, 12810-12820.
7. K. Deng, T. Ren, Y. Xu, S. Liu, Z. Dai, Z. Wang, X. Li, L. Wang and H. Wang, *J. Mater. Chem. A*, 2020, **8**, 5595-5600.
8. C. Zhang, H. Liu, Y. Liu, X. Liu, Y. Mi, R. Guo, J. Sun, H. Bao, J. He and Y. Qiu, *Small Methods*, 2020, **4**, 2000208.
9. G. Meng, H. Tian, L. Peng, Z. Ma, Y. Chen, C. Chen, Z. Chang, X. Cui and J. Shi, *Nano Energy*, 2021, **80**, 105531.
10. Y. Liu, S. Liu, Y. Wang, Q. Zhang, L. Gu, S. Zhao, D. Xu, Y. Li, J. Bao and Z. Dai, *J. Am. Chem. Soc.*, 2018, **140**, 2731-2734.
11. Q. Lu, A.-L. Wang, Y. Gong, W. Hao, H. Cheng, J. Chen, B. Li, N. Yang, W. Niu and J. Wang, *Nat. Chem.*, 2018, **10**, 456-461.
12. S. Liu, Y. Chen, L. Yu, Y. Lin, Z. Liu, M. Wang, Y. Chen, C. Zhang, Y. Pan and Y. Liu, *J. Mater. Chem. A*, 2020, **8**, 25768-25779.
13. Y. Li, J. Chen, J. Huang, Y. Hou, L. Lei, W. Lin, Y. Lian, X. Zhonghua, H.-H. Yang and Z. Wen, *Chem. Commun.*, 2019, **55**, 10884-10887.
14. T. Bhowmik, M. K. Kundu and S. Barman, *ACS Appl. Mater. Interfaces*, 2016, **8**, 28678-28688.