

Electronic Supplementary Information (ESI)

Electroless deposition of RuPd Nanoparticles on porous carbons for hydrogen evolution in acid and alkaline media

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S1. Material Characterizations.

The scanning electron microscope (SEM) images of the samples were obtained by HITACHI S-4800. Transmission electron microscope (TEM) images were received by a JEM2200FS field emission at 200 kV. The morphologies of the catalysts were further characterized by aberration-corrected scanning transmission electron microscopy (HAADF-STEM), equipped with an energy dispersive spectroscopy (EDS) on JEM-ARM300. X-ray photoelectron spectroscopy (XPS) measurements were carried out by a Thermo Scientific K-Alpha photoelectron spectrometer equipped with an Al $K\alpha$ X-ray source. Thermal degradation of the sample was examined with a Rigaku TG-DATA8122 under nitrogen atmosphere. Samples were heated from room temperature to 1000 °C at a rate of 5 °C min⁻¹. The work functions were measured by UV photoelectron spectroscopy (UPS; PHI5000 VersaProbe III SCA) using a He II discharge lamp ($h\nu$, 21.22 eV). The work function was determined using the secondary-electron cutoff (E_{cutoff}) of the UPS using gold as a reference. The position of the Fermi level was calibrated by measuring the Fermi edge of gold. Nitrogen adsorption/desorption isotherms were measured at 77 K by an ASAP 2460 analyzer (Micromeritics, U.S.A). Samples were degassed in a vacuum at 200 °C for 12 h before measurements. Brunauer-Emmett-Teller (BET) method was used to calculate the specific surface area. Raman spectra were recorded on a Invia Reflex. Inductively coupled plasma (ICP) data was obtained by using an Agilent 7800 ICP-MS instrument.

S2. Experimental Section.

Materials. Ruthenium(III) chloride (97%) was purchased from Shanghai Bide pharmatech Co. Ltd. Tannic acid (TA) was purchased from Tianjin Damao Chemical Reagent Factory. 4,4'-

sulfonyldiphenol (BPS) (99.0%, Macklin), Hexachlorocyclotriphosphazene (HCCP) (98%, Macklin), triethylamine (TEA) (99.5%, aladdin), acetonitrile (99%, Macklin), Palladium(II) acetate (99.9%, aladdin) were purchased from Beijing chemical works. Commercial 20% Pt was purchased from J&K. All chemicals were used directly without further purification. Deionized water with a resistivity higher than $18 \text{ M}\Omega \text{ cm}^{-1}$ was used for all experiments.

Synthesis of electrocatalysts.

Synthesis of PSTA. The synthesis route of PSTA was similar to that in the literature¹. Specifically, TA (0.48 g) and TEA (16 mL) were dissolved in acetonitrile (40 mL) and stirred at 35 °C for 3 h in a typical synthesis process. Then, the acetonitrile solution dispersed with HCCP (0.4 g) and BPS (0.4 g) was dropped into the previous solution. The mixed solution was stirred for 12 h, and then transferred to ultrasonic water bath for 1 h. Finally, the precipitated PSTA was separated by centrifugation, washed three times with deionized water, and removed overnight in a vacuum oven at 40 °C.

Synthesis of RuPd/NPSC. In a typical synthesis, PSTA (600 mg) is carbonized for 3 h in a 1000 °C nitrogen atmosphere at a heating rate of 5 °C min⁻¹. The resulting product is thoroughly ground to obtain NPSC. Then, NPSC (40 mg), RuCl₃ (5 mg) and Pd (OAc)₂ (5 mg) were added into deionized water (60 mL) and stirred fully at room temperature (298 K) for 12 h. After filtration separation, the filter cake was washed with 600 mL deionized water and freeze-dried for 8 h at - 40 °C to obtain RuPd/NPSC.

Electrochemical Measurements. All electrochemical tests were carried out on the electrochemical workstation of the general three electrode system (CHI760e, Shanghai Chenhua Instrument Factory, China), in which saturated calomel electrode (SCE) was used as the reference

electrode, a carbon rod was used as the counter electrode, and the electrolyte was 1 M KOH or 0.5 M H₂SO₄ solution². Typically, 3.0 mg of catalyst was dispersed in 600 μ l of isopropanol aqueous solution (300 μ l of isopropanol and 300 μ l of deionized water), followed by 30 μ l of Nafion solution (5wt%, Du Pont). The suspension was sonicated to form a uniform ink. Then, 10 μ l of ink was evenly coated on the glassy carbon surface and dried naturally at room temperature. During HER test, the speed was set at 1600 r min⁻¹ and the scanning rate was 5 mV s⁻¹. All the data were finally calibrated against a reversible hydrogen electrodes.

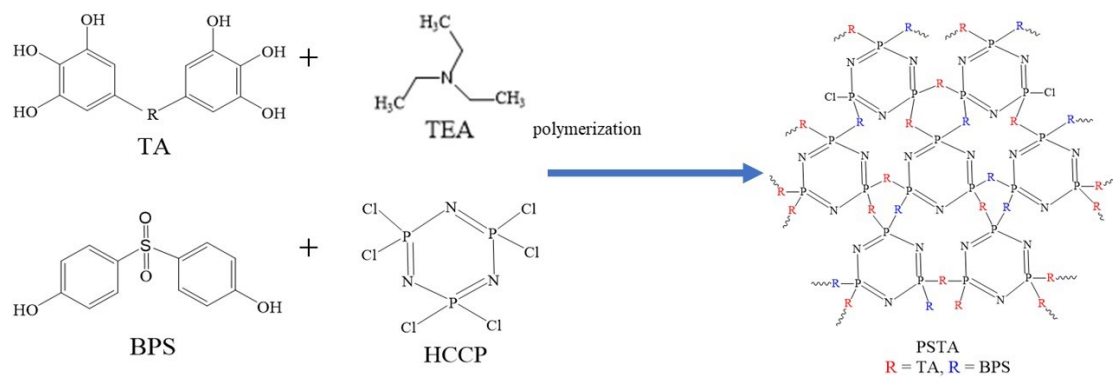


Fig. S1 Schematic diagram of synthesis route of PSTA.

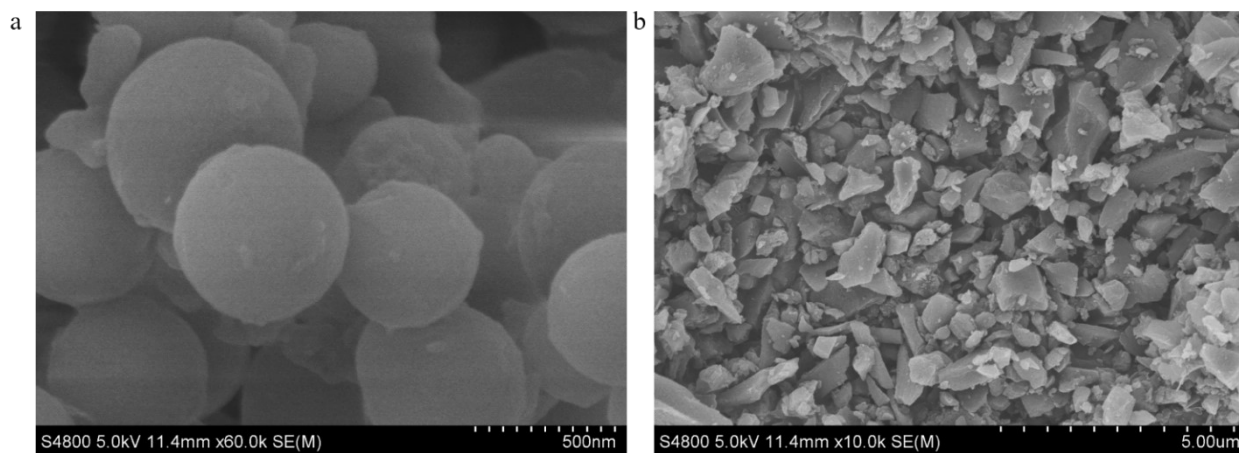


Fig. S2 SEM images of PSTA (a) and NPSC (b).

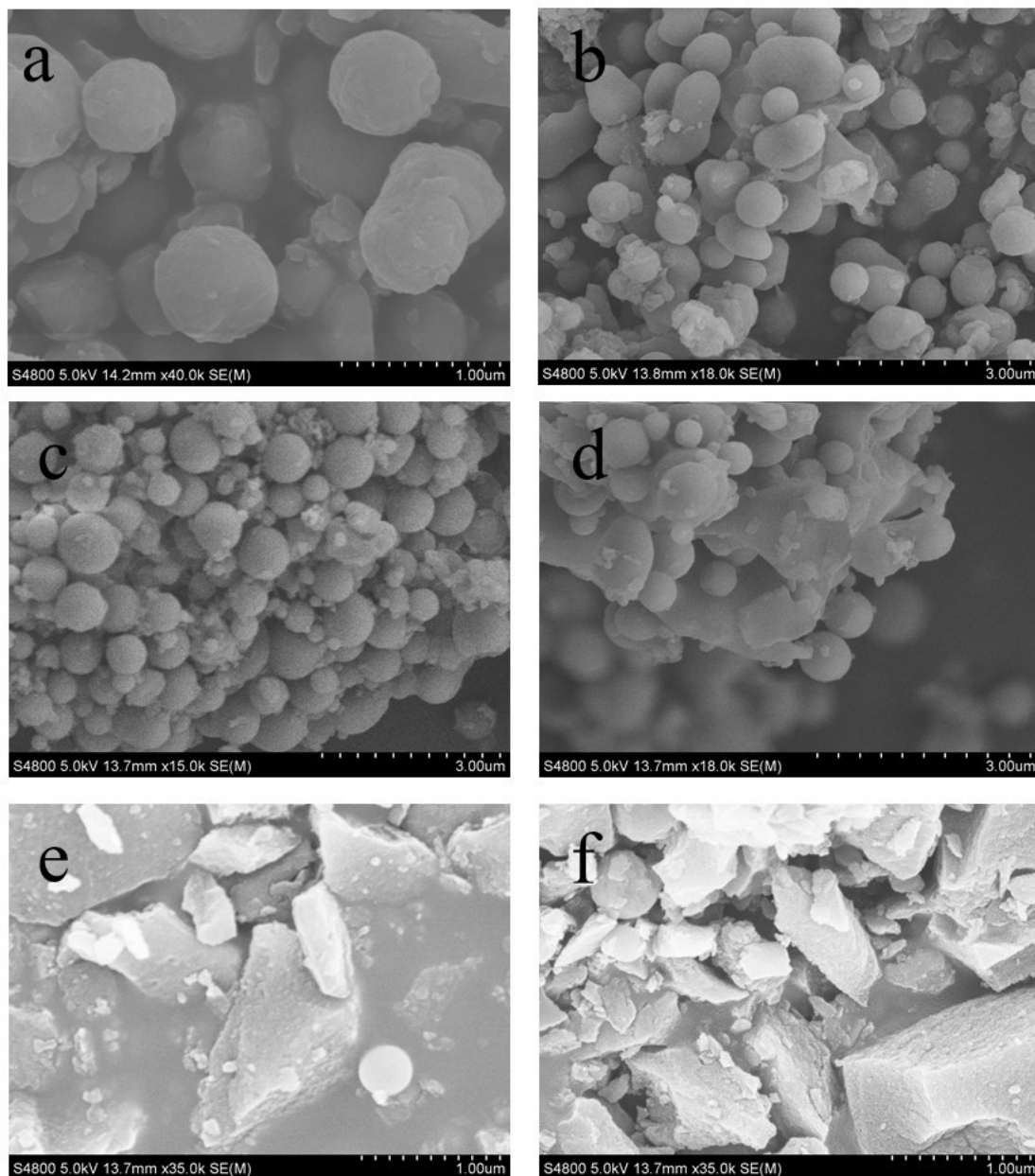


Fig. S3 SEM images of PSTA prepared with different monomer concentrations, (a) and (b) are PSTA_{1x}, (c) and (d) are PSTA_{2x}. (e) and (f) are SEM image of PSTA_{2x} after carbonization at 1000 °C.

Note: We reduced the polymerization monomer concentration of PSTA to 1/2 and 1/4 (named PSTA_{1x} and PSTA_{2x} respectively, as a control, and named the product at the original concentration PSTA_{4x}) to prepare spherical PSTA with smaller diameter. The experimental results show that the spherical structures of PSTA_{1x}, PSTA_{2x} and PSTA_{4x} are all 500 nm in diameter. After carbonization at 1000 °C, the spherical structures of PSTA_{2x} (Figure S3e and S3f) and PSTA_{4x} (Figure S2b)

collapsed and transformed into porous carbon (PSTA_{1x} could not prepare its carbides due to low yield).

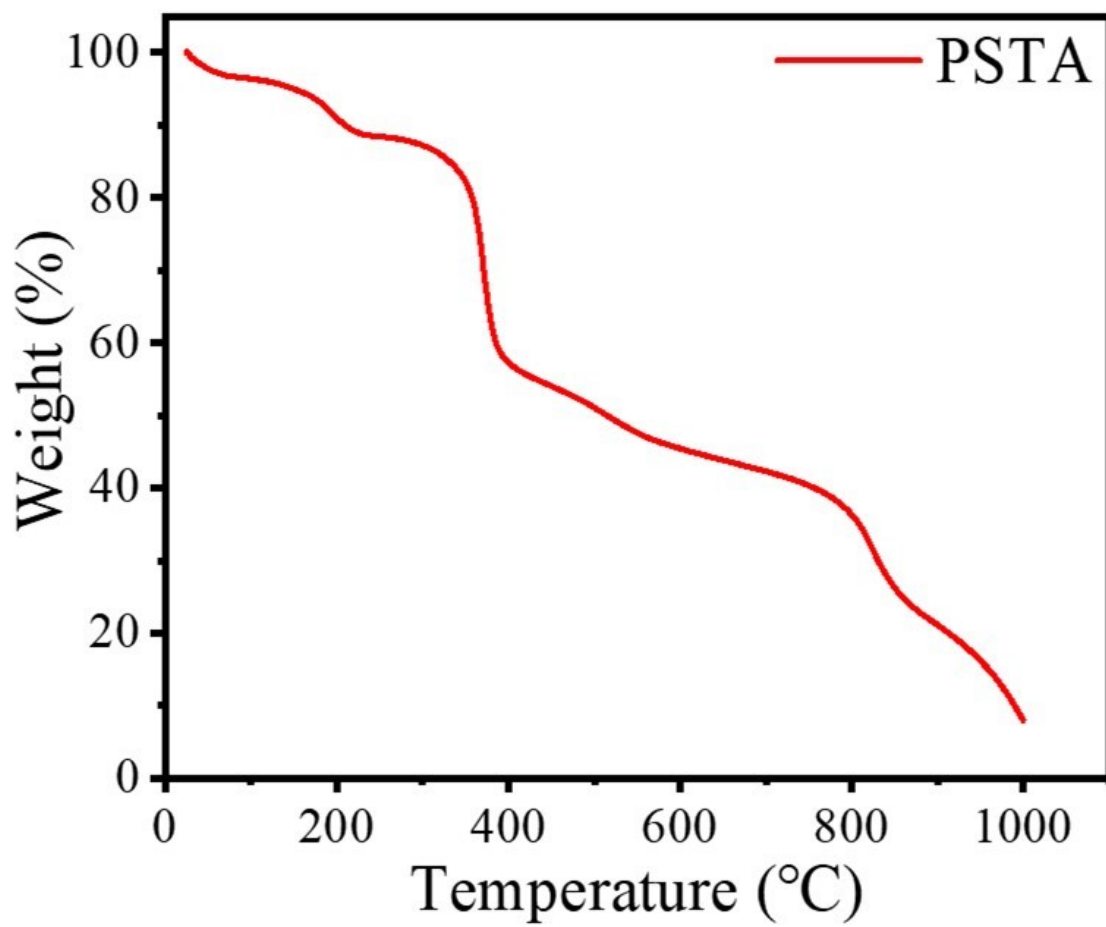


Fig. S4 TGA curves of PSTA.

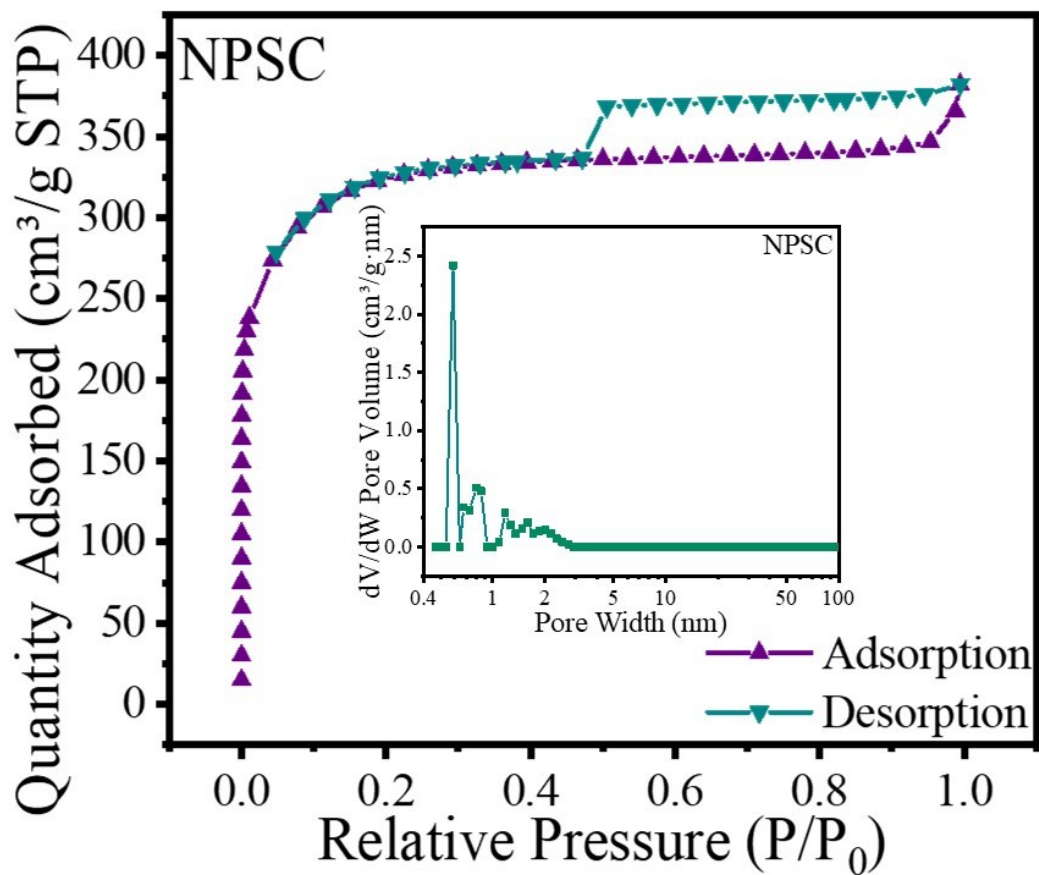


Fig. S5 N₂ sorption isotherms of NPSC. The inside illustration shows the pore size distribution.

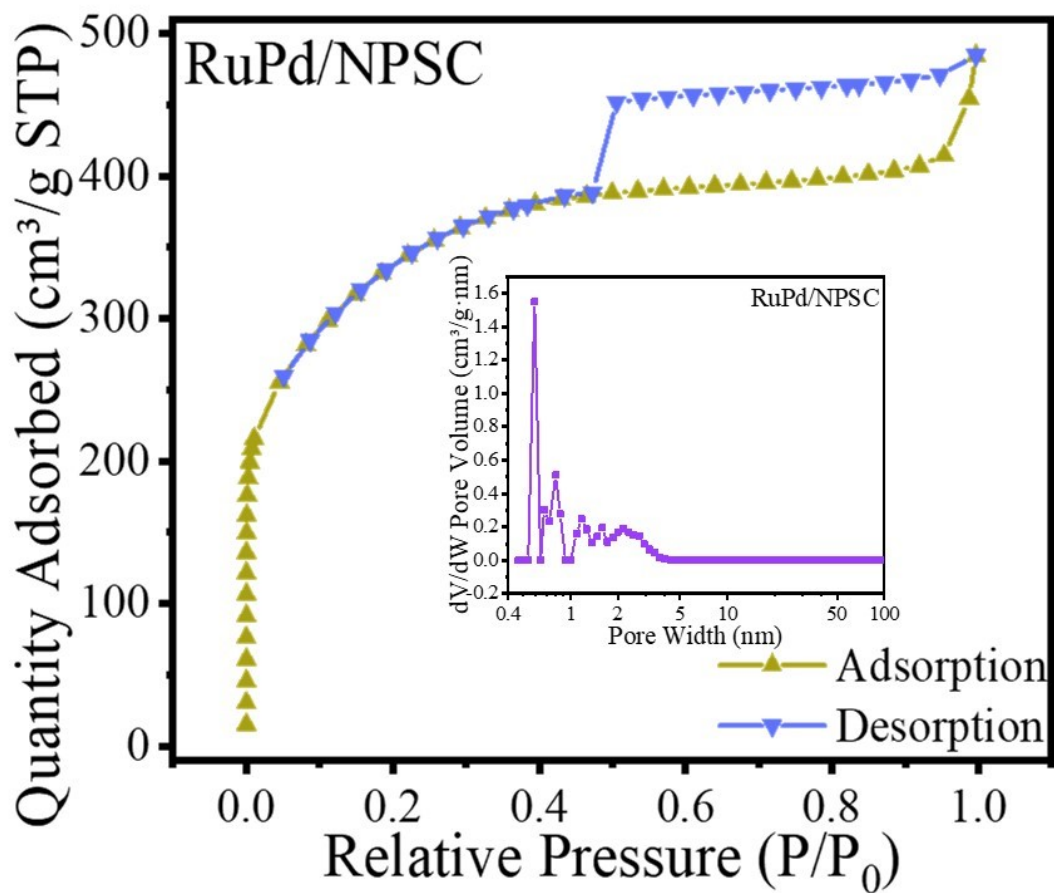


Fig. S6 N₂ sorption isotherms of RuPd/NPSC. The inside illustration shows the pore size distribution.

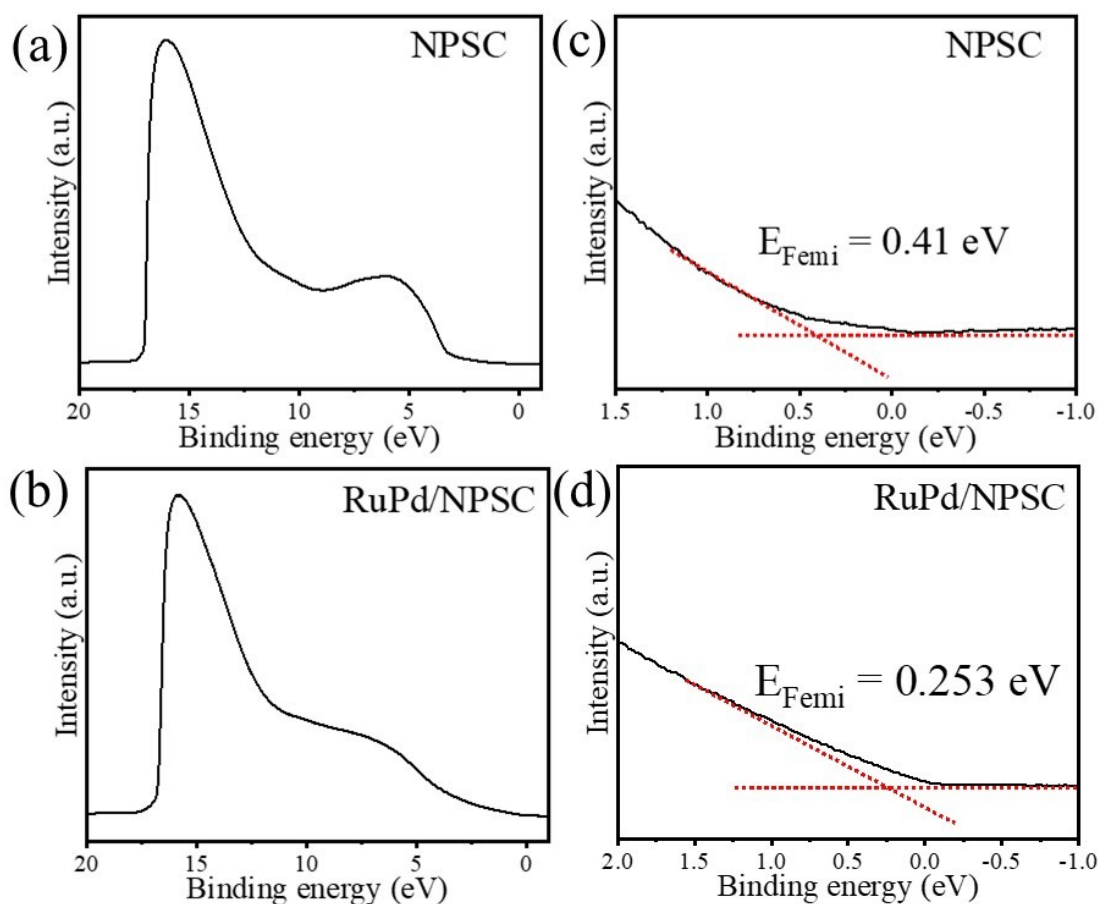


Fig. S7 UPS spectra of NPSC (a) and RuPd/NPSC (b). E_{Fermi} results for NPSC (c) and RuPd/NPSC (d).

Note: The corresponding E_{cutoff} and E_{Fermi} information can be obtained by UPS test of NPSC and RuPd/NPSC respectively. For E_{cutoff} , linearly extrapolate the intersection of the steep drop part of the secondary electronic cutoff edge with the local noise baseline, and the results are shown in Fig. 2e and Fig. 2f in the manuscript. For E_{Fermi} , the initial steep rise part of Fermi edge is linearly extrapolated and its intersection with the background noise baseline is taken. The E_{Fermi} information of NPSC and RuPd/NPSC thus obtained is shown in Fig. S7c and Fig. S7d.

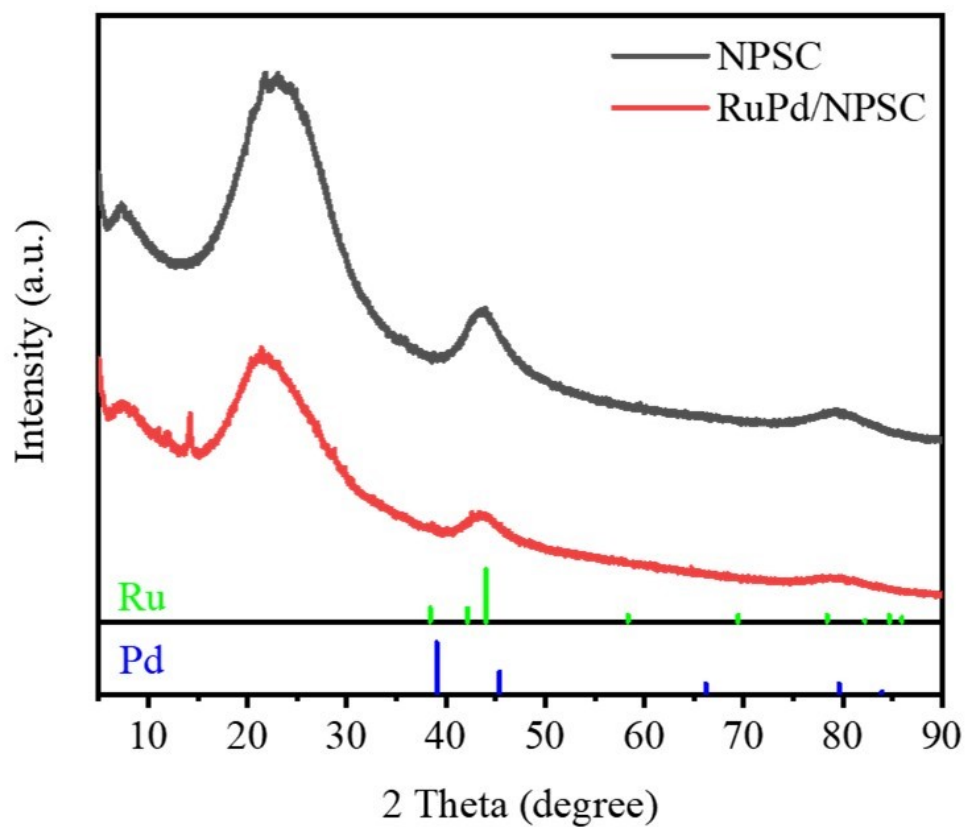


Fig S8 XRD patterns of NPSC and RuPd/NPSC powders. Ru crystal (PDF#89-4903) and Pd crystal (PDF#87-0637) were used as control.

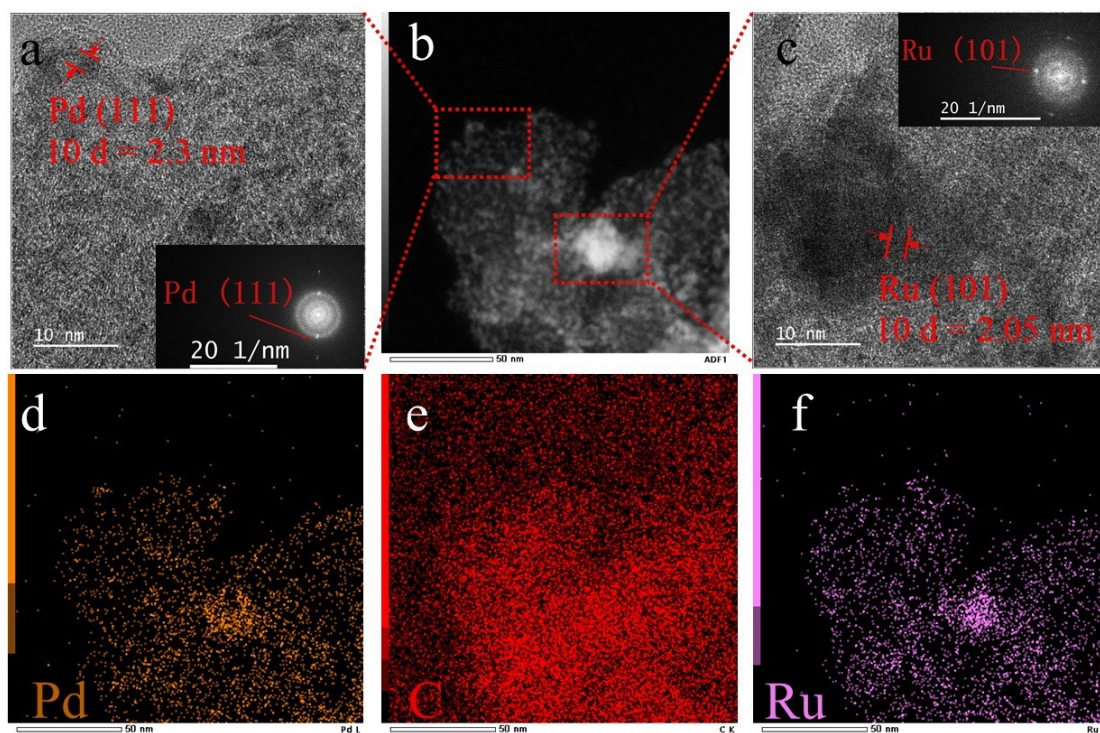


Fig. S9 HRTEM images of Pd nanoparticles (a), RuPd/NPSC (b) and Ru (c) nanoparticles, with the corresponding SAED images in the illustration. (d), (e) and (f) are the element mapping of (b).

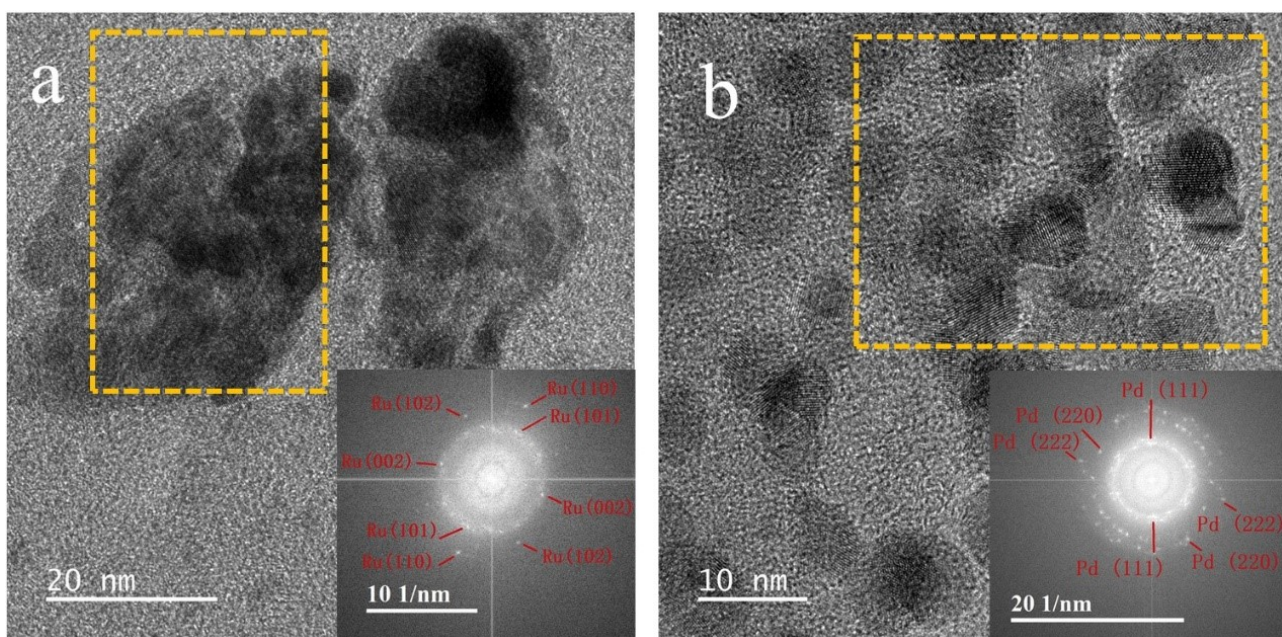


Fig. S10 HRTEM images of RuPd/NPSC. (a) is Ru nanoparticles, (b) is Pd nanoparticles. The illustrations in (a) and (b) are the SAED images of the corresponding selected area, respectively.

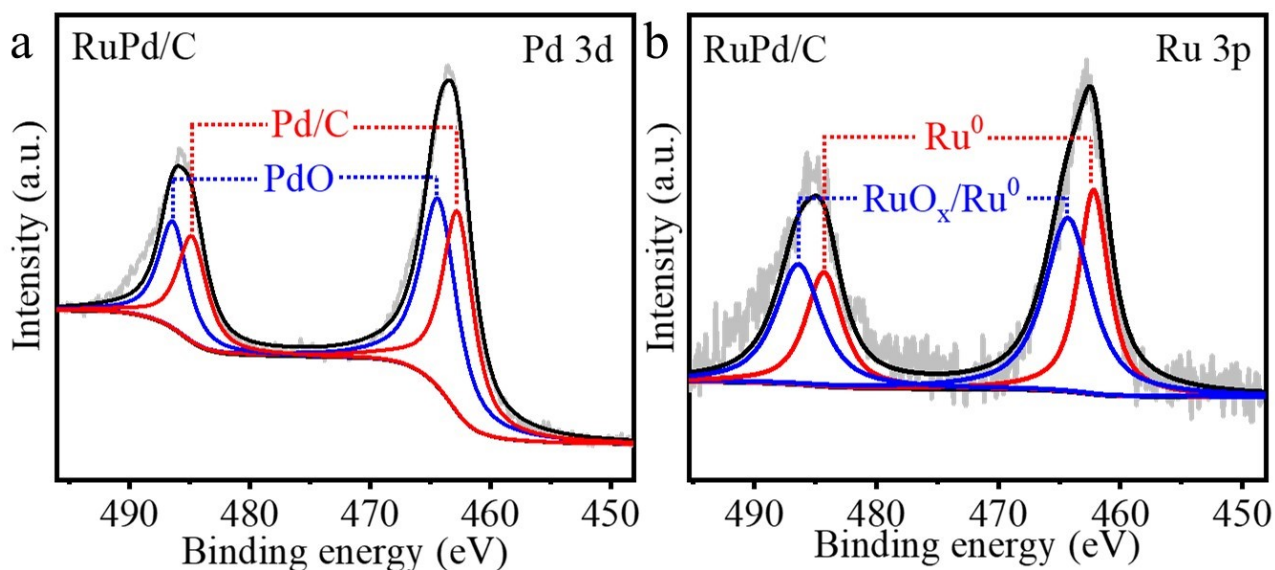


Fig. S11 Fine orbital spectrum of RuPd/C, Pd 3d orbital (a), Ru 3p orbital (b).

Note: In order to verify the electroless deposition ability of carbon substrate again, we used carbon black (acetylene, 100 % compressed, purchased from Alfa Aesar (China) chemical Co. Ltd) as substrate for electroless deposition of RuPd/C as a control experiment (Except for carbon substrate replacement, the experimental procedure is completely consistent with that of RuPd/NPSC).

According to NIST database and existing literatures ((Ref 40: Y.-T. Li, et al. *Fuel*, 2020, **277**, 118243; Ref 41: M. Tang, et al. *ACS Catal.*, 2015, **5**, 3100-3107)), Ru 3p orbit can be deconvoluted into RuO_x/Ru (464.3/486.4 eV) and Ru⁰ (462.2/484.3 eV) peaks. Pd 3d orbit can be deconvoluted into Pd/C peak (336.4/342.0 eV) and PdO peak (337.2/342.8 eV). The above results show that Ru³⁺ and Pd²⁺ are reduced to Ru⁰ and Pd⁰ by electroless deposition on carbon black, accompanied by the coexistence of a small amount of metal oxides. The reduced Ru and Pd also have strong interaction and electron transfer with the substrate. RuPd/C XPS test results were identical with RuPd/NPSC, indicating that the unmodified carbon is not ideally inert and has the ability to reduce metal at room temperature. RuPd/C prepared by carbon black also shows that electroless deposition is universal and is an excellent strategy for preparing precious metal catalysts.

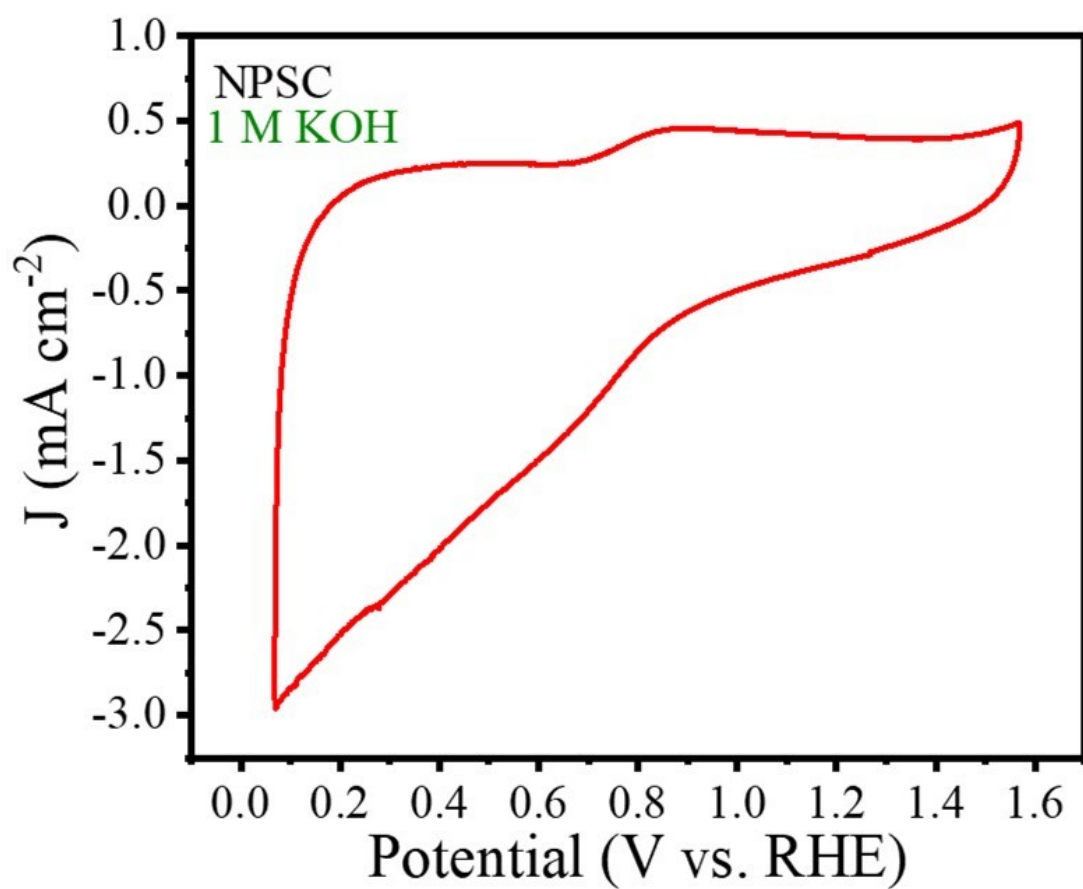


Fig. S12 CV curve of NPSC at 0.06 - 1.56 V in 1 M KOH solution, the scanning rate is 50 mV/s.

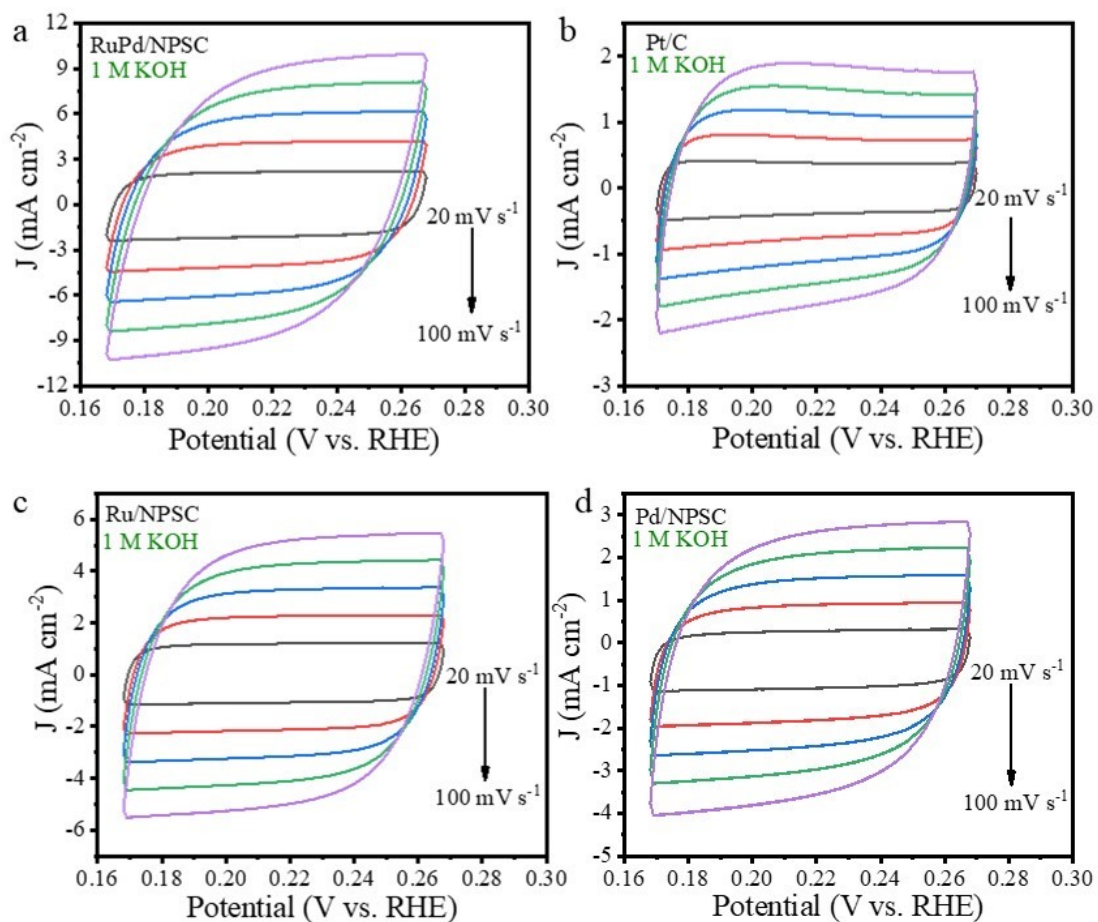


Fig. S13 (a-d) CV curves of RuPd/NPSC, Pt/C, Ru/NPSC and Pd/NPSC at 0.16-0.27 V in 1 M KOH solution, the scanning rate ranging from 20-100 mV/s.

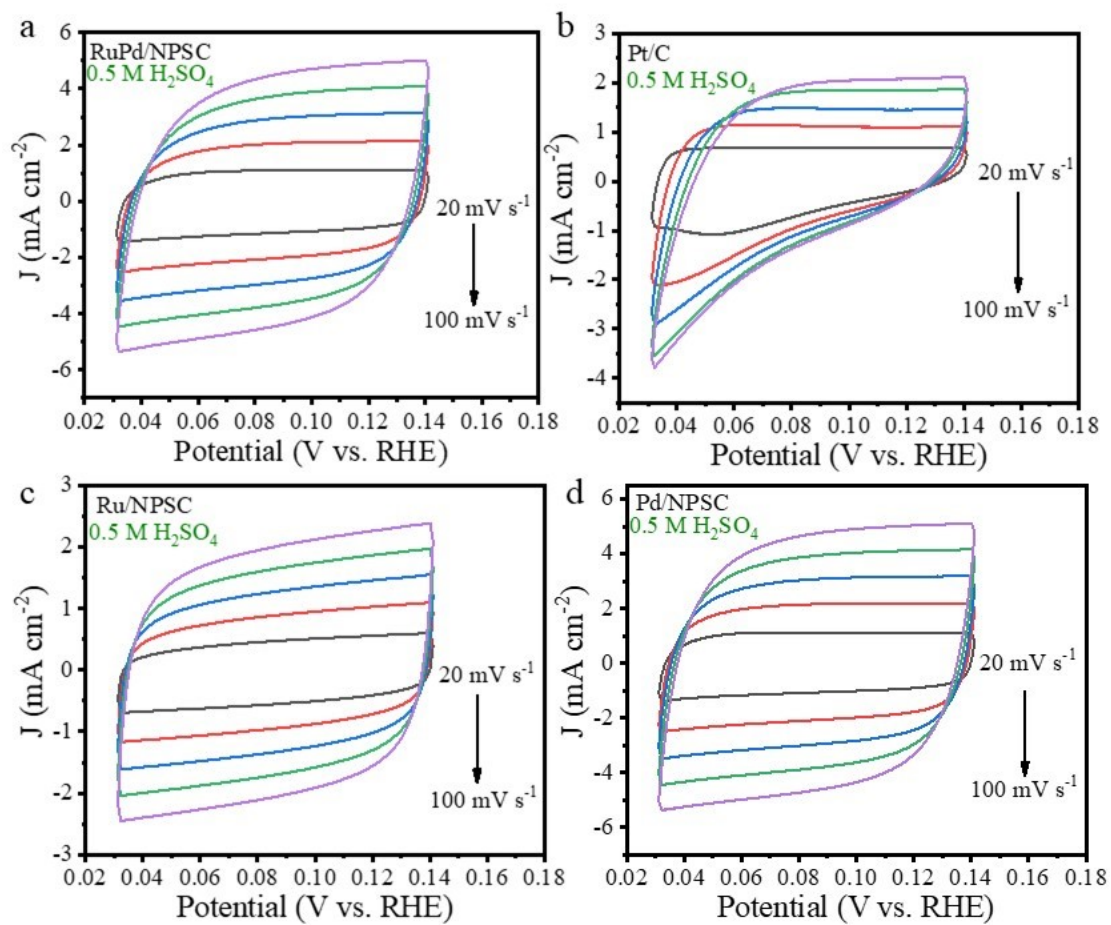


Fig. S14 (a-d) CV curves of RuPd/NPSC, Pt/C, Ru/NPSC and Pd/NPSC at 0.03-0.14 V in 0.5 M H₂SO₄ solution, the scanning rate ranging from 20-100 mV/s.

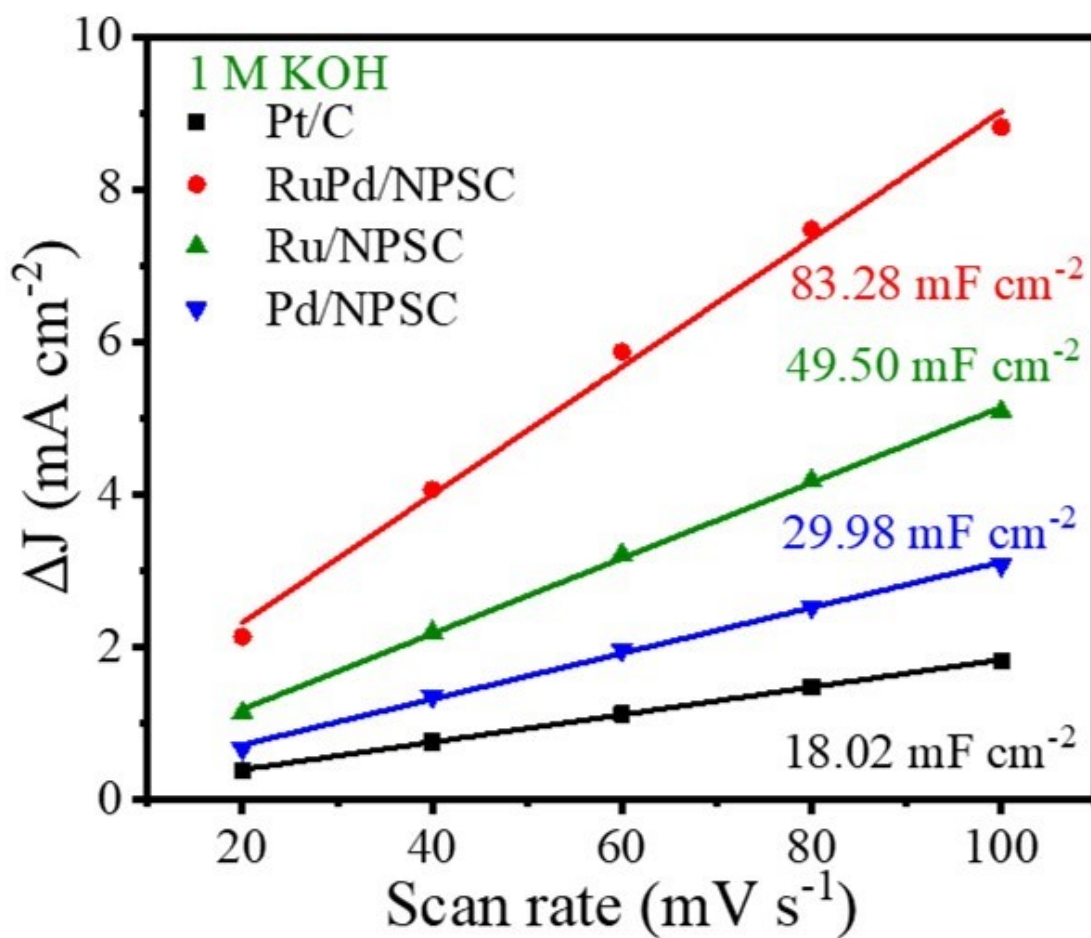


Fig. S15 Difference in current density plotted against scan rate showing the extraction of the double-layer capacitances in 1M KOH solution.

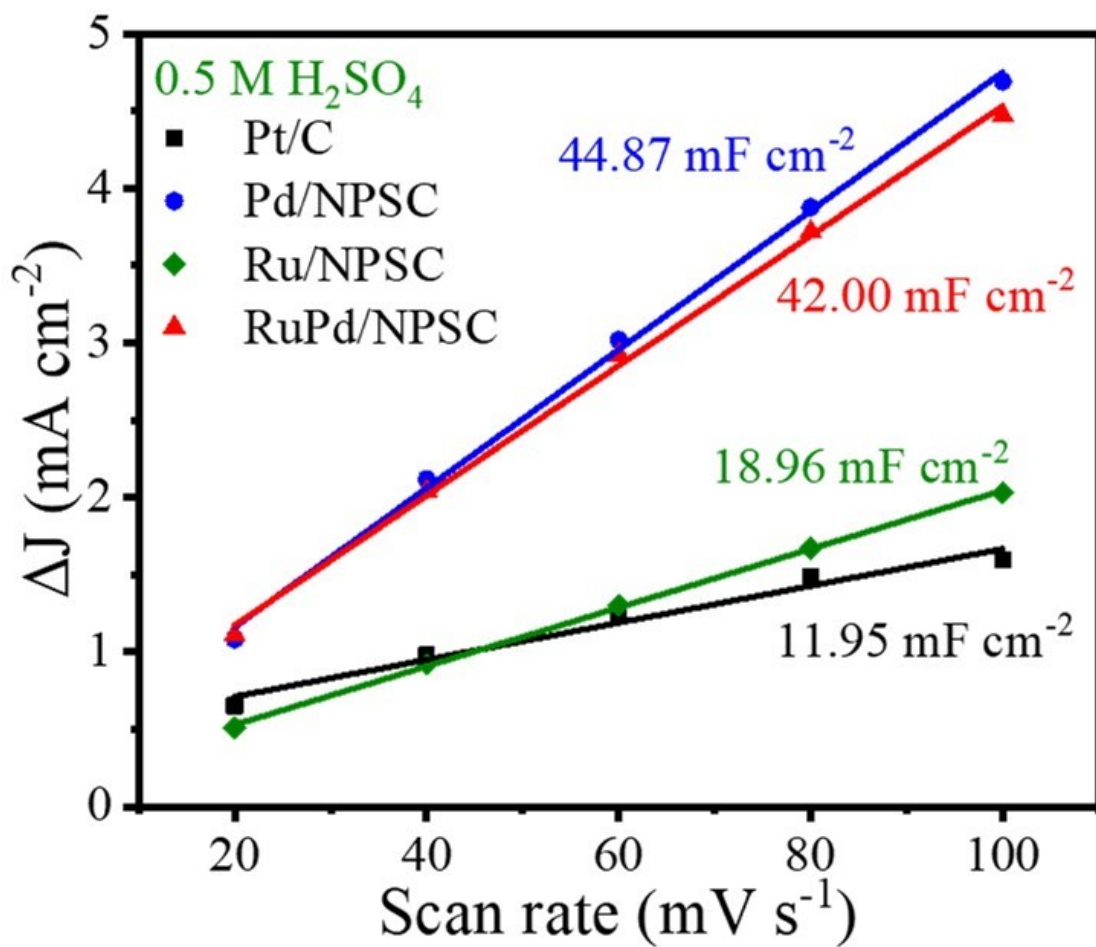


Fig. S16 Difference in current density plotted against scan rate showing the extraction of the double-layer capacitances in 0.5 M H₂SO₄ solution.

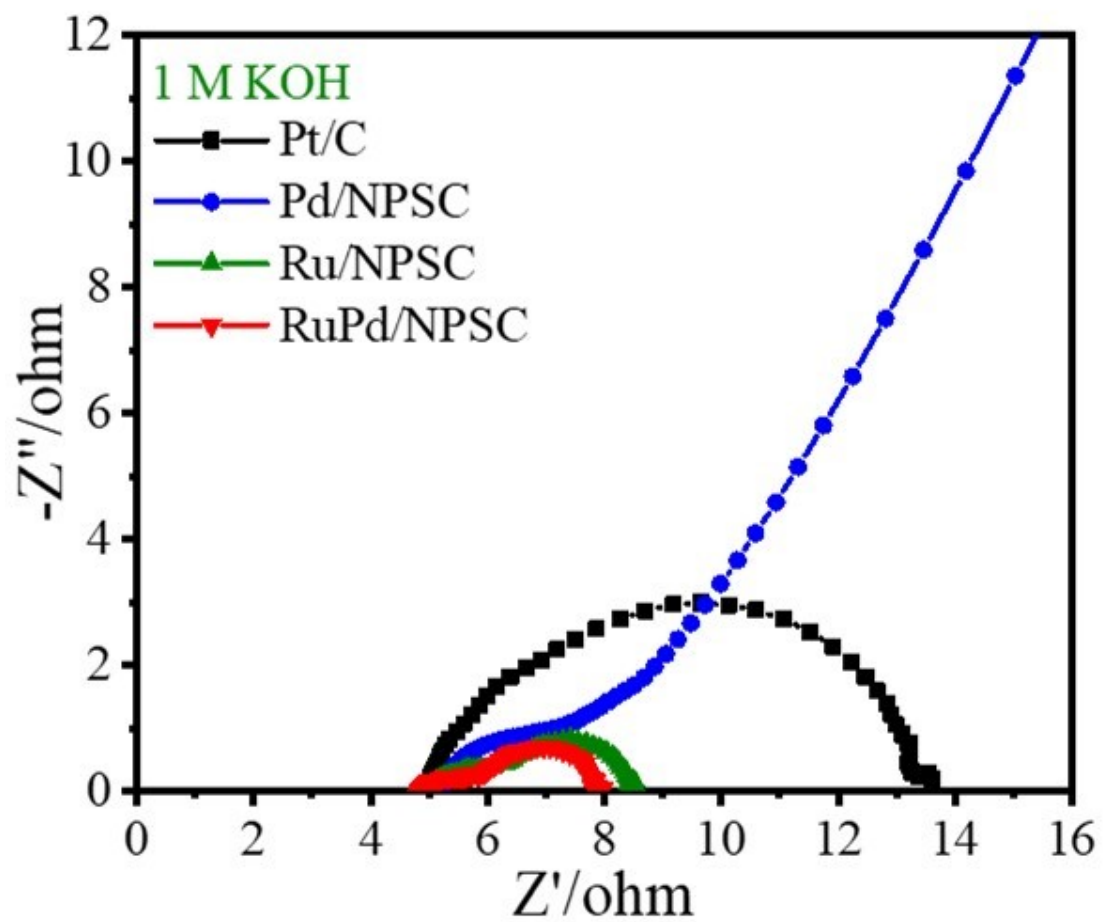


Fig. S17 Nyquist plots of Pt/C, RuPd/NPSC, Ru/NPSC and Pd/NPSC in 1 M KOH solution.

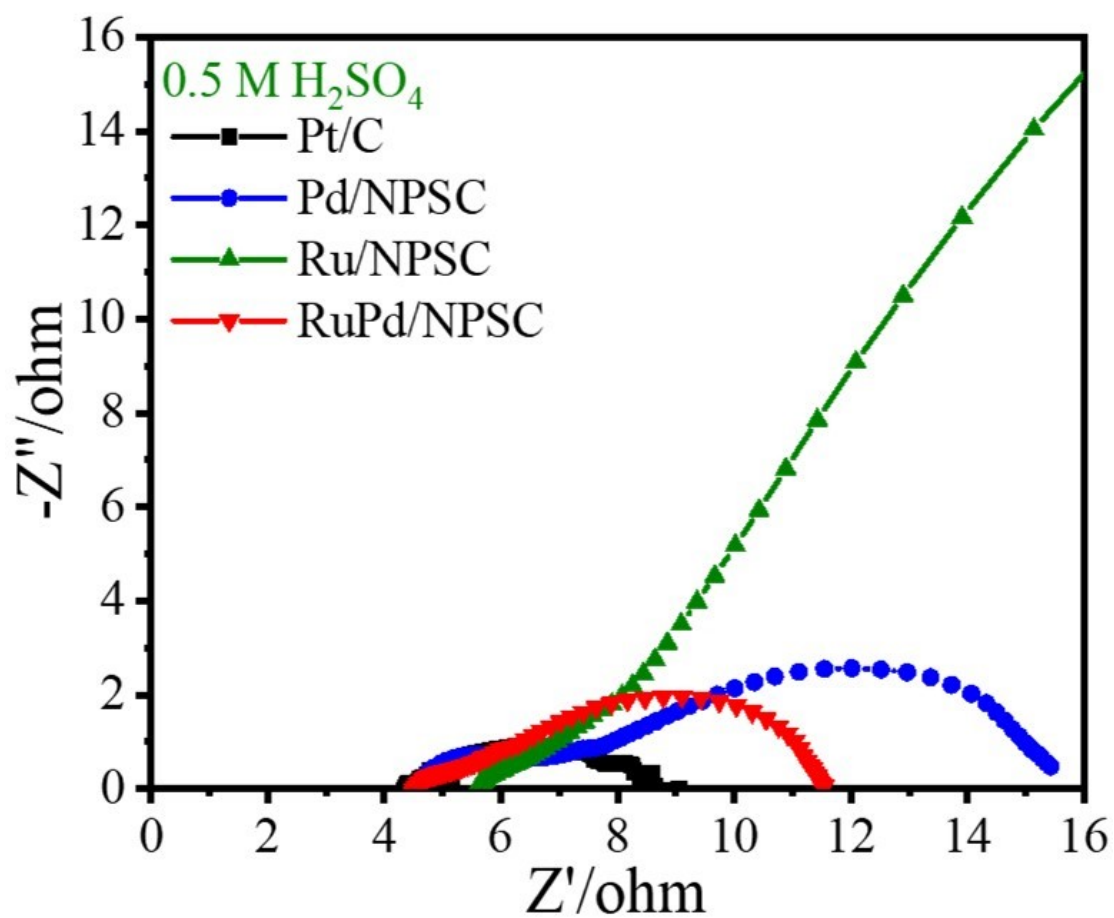


Fig. S18 Nyquist plots of Pt/C, RuPd/NPSC, Ru/NPSC and Pd/NPSC in 0.5 M H_2SO_4 solution.

Table S1 Summary of XPS elements analysis of PSTA, NPSC and RuPd/NPSC.

| Samples | C (at %) | N (at %) | O (at %) | P (at %) | S (at %) | Ru (at %) | Pd (at %) |
|-----------|-------------|-------------|-------------|-------------|-------------|--------------|--------------|
| PSTA | 65.30 | 6.020 | 22.41 | 4.19 | 2.08 | - | - |
| NPSC | 88.26 | 1.87 | 8.35 | 0.84 | 0.67 | - | - |
| RuPd/NPSC | 74.73 | 1.77 | 20.32 | 0.86 | 0.21 | 1.35 | 0.77 |

Table S2 Summary of ICP-MS elements analysis of RuPd/NPSC.

| Sample | Ru (wt %) | Pd (wt %) |
|-----------|--------------|--------------|
| RuPd/NPSC | 2.45 | 2.11 |

References

- S1. X. Wei, D. Zheng, M. Zhao, H. Chen, X. Fan, B. Gao, L. Gu, Y. Guo, J. Qin, J. Wei, Y. Zhao and G. Zhang, *Angew. Chem. Int. Ed.*, 2020, **59**, 14639-14646.
- S2. D. Wang, L. Yang, H. Liu and D. Cao, *J Catal*, 2019, **375**, 249-256.