Supporting Information

Synergistically enhanced hydrogen evolution reaction by ruthenium nanoparticles dispersed on N-doped carbon hollow nanospheres

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**Experimental section**

**Chemicals**

RuCl$_3$·xH$_2$O (M: 225.44) and tetraethyl orthosilicate (TEOS) were obtained from Shanghai Macklin Biochemical Co., Ltd. Poly (sodium 4-styrenesulfonate) (PSS; M$_w$ < 700000 Da) and poly (diallyldimethylammonium chloride) (PDDA; M$_w$ < 500000 Da) were purchased from Alfa Aesar Co. Ltd. Commercial 20% Pt-C was bought from Johnson Matthey. All reagents were utilized without further treatment.

**Synthesis of samples**

**SiO$_2$@PSS.** To prepare the SiO$_2$@PSS composite, SiO$_2$ nanospheres were first prepared by modified stöber approach and selected as hard templates to control the entire morphology throughout the overall synthetic process. Namely, ethanol (100 mL), H$_2$O (6 mL), ammonium hydroxide (6 mL), and TEOS (3 mL) were gradually added together and mechanically stirred for 5 h, then the products were separated by centrifugation at 10000 rpm for 5 min, and washed several times with water and ethanol. Finally, the solid was dried at 80 °C for 6 h under vacuum to obtain SiO$_2$ nanospheres. The resulting SiO$_2$ nanospheres were coated with negative charges according to a self-assembly strategy. In brief, 500 mg of the as-prepared SiO$_2$ nanospheres were added into 100 mL of NaCl solution (0.5 M) and sonicated for 1 h. After the addition of PDDA (750 mg), the suspension was stirred continuously for 1 h and then separated by centrifugation at 8000 rpm for 7 min, washed three times by H$_2$O. Subsequently, the obtained sample was dispersed into 100 mL of NaCl solution (0.5 M) and sonicated for 1 h. Then, 0.15 g PSS was added into the above solution and stirred continuously for 1 h. After that, the excess PSS was removed by three repeated centrifugation/wash cycles. By means of repeating the abovementioned method, the as-formed nanospheres were decorated sequentially with PDDA, and PSS to obtain nanospheres with negative charges (denoted as SiO$_2$@PSS).

**Ru@NCHNSs.** In a typical procedure, 300 mg of the SiO$_2$@PSS nanospheres were well-dispersed into 10 mL of water by sonicating for 30 min. Then, 3.3 mL of RuCl$_3$ solution (30 mg mL$^{-1}$) was added and kept stirring for 4 h. Afterward, 155 mg of histidine was introduced, further stirring for 5 h. The resultant suspension was collected and dried in
a vacuum oven at 90 °C (SiO$_2$@RuCl$_3$-His). Next, the as-prepared sample was carbonized at different temperatures (700, 800, and 900 °C) under the Ar atmosphere for 4 h (SiO$_2$@Ru@NCNSs-T, $T = 700, 800, \text{ and } 900$), respectively. After heating treatment, the product was etched by HF solution to remove the SiO$_2$ templates, further yielding hollow carbon nanospheres (designed as Ru@NCHNSs).

**Ru@NC.** The Ru@NC catalyst was also synthesized through the identical procedure except that the SiO$_2$ nanospheres were not been added.

**NCHNSs.** The NCHNSs sample was also prepared by the similar method without adding RuCl$_3$.

**Instruments**

The morphologies and structural features were examined by scanning electron microscope images (SEM, JSM-7600F) at an acceleration voltage of 10 kV and high-resolution transmission electron microscopy (HRTEM, JEM-2100F) at an accelerating voltage of 200 kV. The energy-dispersive X-ray spectroscopy (EDX) was taken on JSM-5160LV-Vantage typed energy spectrometer. To determine the chemical composition of the as-synthesized catalysts, the inductively coupled plasma atomic emission spectroscopy (ICP-AES) were carried out on a Prodigy Leeman ICP-AES spectrometer. The powder X-Ray diffraction (XRD) patterns were recorded on a D/max 2500VL/PC diffractometer (Japan) equipped with graphite monochromatized Cu Kα radiation ($\lambda = 1.54060$ Å). Corresponding work voltage and current is 40 kV and 100 mA, respectively. X-ray photon spectroscopy (XPS) was recorded by a scanning X-ray microprobe (PHI 5000 Verasa, ULAC-PHI, Inc.) using Al kα radiation and the C1s peak at 284.8 eV as internal standard. The nitrogen adsorption-desorption experiments were operated at 77 K on a Micromeritics ASAP 2050 system. The pore size distributions were measured by Barret-Joyner-Halenda (BJH) model. Prior to the measurement, the samples were degassed at 150 °C for 10 h.

**Electrochemical Measurements**

Electrochemical tests were assessed in a N$_2$-saturated 1.0 M KOH solution using a three-electrode system. A glassy carbon electrode (GCE, 3 mm in diameter), saturated
calomel electrode (SCE) and a graphite rod were chosen as the working electrode, reference electrode and the counter electrode, respectively. 4 mg of the catalyst was well-dispersed in 1.8 mL of ethanol and 0.2 mL Nafion by ultrasonic for 30 min. Then, 5 μL of the uniform ink was decorated on a glassy carbon electrode as the working electrode, further drying at 40 °C. The mass loading on the glassy carbon electrode is 0.142 mg cm⁻². Linear sweep voltammetry (LSV) was collected at a scan rate of 2 mV s⁻¹ with 95% iR drop compensation. All of these potentials were calibrated relative to reversible hydrogen electrode (RHE) after transformation \( E_{\text{RHE}} = E_{\text{SCE}} + 0.059 \text{pH} + E^{0}_{\text{SCE}} \). In 1.0 M KOH solution, \( E_{\text{RHE}} = E_{\text{SCE}} + 1.0698 \). Electrochemical active surface area (ECSA) was measured by the cyclic voltammogram (CV) curves with in the region of 0.1198-0.2198 V vs. RHE at various scan rates (20-200 mV s⁻¹). The electrochemical impedance spectra (EIS) methods were evaluated in the range of 1000 kHz-0.1 Hz with an amplitude of 10 mV.

The study for full water splitting was investigated with a two-electrode system in 1.0 M KOH solution. The applied voltage window was from 0 to 2.0 V. Each catalyst (2 mg, Ru@NCHNSs, Ru@NC, or commercial 20% Pt-C) was added into 1 mL of ethanol/Nafion mixture solution (v:v = 9:1) and sonicated for at least 30 min, respectively. Subsequently, the ink was coated on the surface of a Ni foam (1×1 cm²), which functioned as the cathode electrode. In parallel, the anode electrode was designed by the same method using commercial IrO₂ as catalyst.

The mass activity \( (\text{mA mg}^{-1}) \) values of different samples were calculated from the electrocatalyst loading \( m \) (0.01 mg).

\[
\dot{j}_{\text{max activity}} (\text{mA mg}^{-1}) = \frac{I \text{ (mA)}}{m \text{ (mg)}}
\]

Where,

\( I \text{ (mA)} \) = the measured current

\( m \text{ (mg)} \) = the electrocatalyst loading (0.01 mg)
S1. Figures in Supporting Information

**Fig. S1** SEM and TEM images of SiO$_2$ NSs (a1, a2), SiO$_2$@RuCl$_3$-His NSs (b1, b2), and SiO$_2$@Ru@NCNSs (c1, c2).

First, PSS is coated on the surface of the as-prepared SiO$_2$ nanospheres through a self-assembly approach to fabricate negatively charged SiO$_2$@PSS nanospheres. Next, the SiO$_2$@PSS nanospheres are successively wrapped with Ru$^{3+}$ and histidine, denoted as SiO$_2$@RuCl$_3$-His. Then, the SiO$_2$@RuCl$_3$-His nanospheres are converted into SiO$_2$@Ru@NCNSs nanospheres during heating treatment. Last, the SiO$_2$ template can be selectively etched with HF solution to achieve hollow NCHNSs-anchored Ru NPs nanocomposite. Scanning electron microscope (SEM) image (Fig. S1a) reveals that the SiO$_2$ nanospheres synthesized by a modified stöber method are greatly homogeneous with a mean size of ~ 380 nm, proven by the corresponding transmission electron microscope (TEM) image (Fig. S1b). Through strong electrostatic attractions, Ru$^{3+}$ ions are adsorbed onto the negatively charged SiO$_2$@PSS nanospheres. Then, histidine molecules can combine with the Ru$^{3+}$ ions by means of coordination actions. The SEM and TEM images of SiO$_2$@RuCl$_3$-His show that spherical structure is perfectly retained but the
corresponding surface of the as-formed nanospheres becomes slightly rough (Fig. S1b). After annealing at 800 °C, the His coating is transformed into N-doped carbon nanospheres, while the Ru$^{3+}$ ions are in situ reduced to ultrafine Ru NPs, yielding the SiO$_2$@Ru@NCNSs nanocomposite. As displayed in Fig. S1c, it is obviously seen that the sphere-like shape is well preserved without visible change in morphology. Finally, the SiO$_2$ cores are completely etched by HF solution, further leading to the production of highly dispersed Ru NPs anchored on 3D N-doped carbon hollow nanospheres.
**Fig. S2** The particle-size histogram of Ru@NCHNSs.
Fig. S3 HRTEM image of Ru@NCHNSs.
Fig. S4 EDX spectra of Ru@NCHNSs.
**Fig. S5** The pore size distribution calculated by BJH method according to the N$_2$ sorption isotherm.
**Fig. S6** (a) C 1s + Ru 3d and (b) O 1s XPS spectra of Ru@NCHNSs.

As displayed in the C 1s + Ru 3d spectrum (Fig. S6a), the peaks at 284.8 and 286.4 eV are ascribed to C-C/C=C and C-N. The binding energies at 280.5 and 284.7 eV correspond to Ru 3d$_{5/2}$ and Ru 3d$_{3/2}$ of metallic Ru. Meanwhile, the other peaks at 280.9 and 285.3 eV are attributed to Ru 3d$_{5/2}$ and Ru 3d$_{3/2}$ of RuO$_2$. The high-resolution O1s spectrum is also deconvoluted into three peaks at 530.3 eV (Ru-O), 531.2 eV (O-H), and 532.6 eV (C=O), implying traces of Ru oxide on the surface of the obtained Ru@NCHNSs.
Fig. S7 N1s XPS spectrum of NCHNSs.
The morphology and structural characterizations of Ru@NC were studied by TEM and PXRD, shown in Fig. S8. In sharp contrast, it is clear that numerous larger-sized Ru NPs are randomly distributed in the carbon matrix. Consequently, this result undoubtedly proves that the SiO$_2$ nanosphere as a template plays a crucial role in the fabrication of NCHNS, which contributes to the uniform distribution and excellent stabilization of small-sized Ru NPs.
Fig. S9 (a) $\eta_{10}$ data and (b) calculated mass activity of Ru@NC, Ru@NCHNSs, and 20% Pt-C, respectively.
Fig. S10 (a) TEM image and (b) PXRD pattern of Ru@NCHNSs after the stability test.
In general, the pyrolysis temperature is an important factor for the synthesis of carbon materials. Consequently, the catalytic activities of Ru@NCHNSs obtained at 700, 800, and 900 °C were systematically pre-investigated. As exhibited in Fig. S11, the hybrid synthesized at 800 °C presents the lowest overpotential ($\eta_{10}$) at the current density of 10 mA cm$^{-2}$, and the smallest Tafel slope among the three products, implying the best electrocatalytic activity for the HER. Hence, 800 °C is considered as an ideal pyrolysis temperature in the work.
To disclose the role of Ru active sites for the HER, potassium thiocyanate (KSCN) was added into N₂-saturated 1.0 M KOH solution, because SCN⁻ ions are regarded as poisoning species to metal active sites. As expected, the HER activity of Ru@NCHNSs is drastically decreased after adding SCN⁻ ions into the solution, as proven by the largely negative shift of the onset potential and η₁₀ (Fig. S12a). Furthermore, a sharp jump of current density from 10 to 2.05 mA cm⁻² is obviously seen at t = 200 s in the chronoamperometry (CA) curve (Fig. S12b). Due to the introduction of SCN⁻, the Ru sites are attacked and poisoned, further leading to inferior HER activity. As a result, we conclude that Ru NPs should be the active sites of the Ru@NCHNSs catalyst.
### S2. Table in Supporting Information

**Table S1** Comparison of electrocatalytic HER activity in 1.0 M KOH for Ru@NCHNSs with other HER electrocatalysts.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Tafel slope [mV dec$^{-1}$]</th>
<th>$\eta_{10}$ (mV)</th>
<th>Reference</th>
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<tr>
<td>Ru@NCHNSs</td>
<td>32.7</td>
<td>28.8</td>
<td>This work</td>
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<tr>
<td>IrP$_2$@NC</td>
<td>50</td>
<td>28</td>
<td><em>Energy Environ. Sci.</em>, 2019, 12, 952.</td>
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<tr>
<td>N-Co$_2$P/CC</td>
<td>51</td>
<td>34</td>
<td><em>ACS Catal.</em>, 2019, 9, 3744.</td>
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<tr>
<td>Mo$_2$C@NC@Pt</td>
<td>57</td>
<td>47</td>
<td><em>ACS Appl. Mater. Interfaces</em>, 2019, 11, 4047.</td>
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<tr>
<td>Ni$_3$P-Cu$_3$P/NiCuC</td>
<td>177</td>
<td>78</td>
<td><em>ACS Catal.</em>, 2019, 9, 6919.</td>
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<tr>
<td>Ni@Ni$_3$P-Ru HNRs</td>
<td>31</td>
<td>41</td>
<td><em>J. Am. Chem. Soc.</em>, 2018, 140, 2731.</td>
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