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Facet-controlled hollow Rh$_2$S$_3$ hexagonal nanoprisms as highly active and structurally robust catalysts toward hydrogen evolution reaction

Hydrogen evolution reaction (HER) requires highly efficient and non-deteriorating electrocatalysts able to operate under the harsh operating conditions of the water splitting process. We developed a hollow Rh$_2$S$_3$ nanocage and demonstrated its very high activity and excellent structural durability toward HER in acidic conditions, highlighting the potential usefulness of metal sulfide hollow nanostructures as robust electrocatalysts in water splitting.

As featured in:

Facet-controlled hollow Rh$_2$S$_3$ hexagonal nanoprisms as highly active and structurally robust catalysts toward hydrogen evolution reaction

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Developing highly active and structurally robust electrocatalysts for hydrogen evolution reaction (HER) is of paramount importance for sustainable and clean production of hydrogen. Metal sulphides exposing catalytically active sites, in particular, have been actively pursued as advanced HER catalysts. Herein we report high-performance Rh$_2$S$_3$-based HER catalysts with excellent activity and durability. Hollow Rh$_2$S$_3$ hexagonal nanoprisms with controlled size and thickness could be conveniently prepared by one-step formation of core–shell nanoprisms followed by the etching of the core, and they show high surface areas and highly exposed edge sites. The hollow Rh$_2$S$_3$ nanoprisms exhibit very high HER activity and excellent stability under harsh acidic conditions.

Highly efficient and economically viable production of hydrogen represents a key element in realizing hydrogen economy. While current hydrogen production technologies depend prevalently on the hydrocarbon reforming and methane partial oxidation, the direct conversion of water into hydrogen by electrolysis is considered as one of the most sustainable methods for hydrogen generation. Water electrolysis, when coupled with renewable energy sources such as solar or wind energy, can produce hydrogen with unparalleled capacity and carbon-neutral nature. An essential prerequisite for efficient water electrolysis is the development of highly active catalysts with structural and compositional robustness. Among various catalytic systems, metal sulphides have shown superb catalytic activities toward hydrogen evolution reaction (HER). Hence, a significant effort has been devoted to control the morphology of metal sulphide catalysts to preferentially expose catalytically active sites.

Nanoparticle-based catalysis has witnessed a great advance in recent years. The control of size, shape, and composition of colloidal nanoparticles has enabled the systematic investigation of critical factors responsible for activity and selectivity of many important catalytic transformations. Furthermore, advances in nanoparticle synthesis allowed for the preparation of nanoparticles with previously unprecedented, complex morphologies, including nanoscale hollow and framework structures. These nanoparticle-based catalysts have been prepared by exploiting the nanoscale Kirkendall effect, galvanic replacement reaction, cation exchange reaction, etc. While hollow nanoparticles of metals

Broader context

Hydrogen economy is critically dependent on the efficient and economically viable production of hydrogen. Among various hydrogen production technologies including hydrocarbon reforming and methane partial oxidation, direct conversion of water into hydrogen by electrolysis appears to be the most sustainable method, when coupled with renewable energy sources such as solar or wind energy. In water hydrolysis, the development of highly active catalysts with structural and compositional robustness is most required for the hydrogen evolution reaction (HER). Shape controlled Pt nanoparticles are theoretically most efficient catalysts, but they are not immune from the structural deformation during catalysis and thus incurred performance deterioration. Therefore, there is a strong demand for structurally robust, yet highly efficient nanocatalysts for HER. Rhodium sulphide is particularly promising as a catalyst material due to its excellent phase stability under harsh acidic conditions, which are commonly employed for HER. In this work, we report the synthesis of unprecedented hollow rhodium sulphide nanoparticles with well-defined crystalline facets, which show very high activity and excellent structural durability toward HER.
and metal oxides with a variety of composition have been intensively investigated, the studies on metal sulphide nanoparticles with a hollow shape have been very limited. Furthermore, hollow metal sulphides with well-defined shape and facets have been rarely reported, and little is known for the facet-stabilization mechanism and growth kinetics of them.

In this work, we report the synthesis of hollow rhodium sulphide nanoparticles with well-defined crystalline facets, which show very high activity and excellent durability toward HER. We could prepare the hollow nanoparticles via one-step formation of core–shell nanoparticles followed by selective etching of the core. This method provides a convenient access to hollow, crystalline nanoparticles, which is distinguishable from previously reported routes and cation exchange reactions. As illustrated in Scheme 1, including the Kirkendall effect-driven, galvanic replacement, which is distinguishable from previously reported routes provides a convenient access to hollow, crystalline nanoparticles, particle followed by selective etch in going of the core. This method provides a convenient access to hollow, crystalline nanoparticles, which is distinguishable from previously reported routes.

Subsequent removal of the Cu1.94S phase by acid etching is also indicated by the X-ray diffraction (XRD) patterns taken at 2 min of reaction were analysed by EDS elemental mapping as shown in Fig. S1 (ESI†); the XRD signals corresponding to Cu1.94S are selectively diminished after the core etching of Cu1.94S@Rh2S3.

In order to better understand the formation process of Cu1.94S@Rh2S3 nanoprism, the reaction intermediates obtained at 2 min of reaction were analysed by EDS elemental mapping as well as by TEM images as shown in Fig. S3 (ESI†). The hexagonal nanoparticle shapes are already observable at this early stage of reaction. The major components of these hexagonal nanoparticles are Cu and S and very little Rh component, which is smaller than the detection limit, is observed. However, the final structures in Fig. S1 (ESI†) clearly show the inner Cu component and the shell Rh component. Therefore, it is envisaged that the fast forming Cu1.94S nanoparticles act as self-generated templates for the subsequent growth of the Rh2S3 phase. Also, the final Cu1.94S@Rh2S3 nanoparticle is much thicker than the in situ formed Cu1.94S nanoparticle. This seems to indicate that heteroepitaxial growth is a dominant route for the formation of the Rh2S3 phase, although the galvanic exchange of Cu by Rh cannot be completely ruled out as the growth mechanism of the initial Rh2S3 layer.

Result and discussion

Representative transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images with fast Fourier transformation (FFT) patterns of Cu1.94S@Rh2S3 and Rh2S3 nanoparticles are shown in Fig. S1 (ESI†) and Fig. 1, respectively. The monodisperse size distribution and the hexagonal plate shape are clearly observed for both Cu1.94S@Rh2S3 and hollow Rh2S3 nanoparticles. The size of hollow Rh2S3 nanoparticles is slightly reduced from that of Cu1.94S@Rh2S3 after etching; the average sizes of hexagonal Cu1.94S@Rh2S3 nanoparticles and hollow Rh2S3 nanoparticles are 88.0 ± 4.1 nm and 84.1 ± 4.0 nm, respectively, which are measured from diagonal point to point. The average thickness of 19.3 ± 1.5 nm for Cu1.94S@Rh2S3 is also decreased to 17.0 ± 2.2 nm for Rh2S3. The hexagonal faces of orthorhombic Rh2S3 nanoprism are enclosed by (110) facets. The six sides of hexagonal nanoparticles are found to be (211) and (211) planes as verified by the HRTEM image and the FFT pattern. The elemental mapping images by energy-dispersive X-ray spectroscopy (EDS) shown in Fig. S1 (ESI†) and Fig. 1d and e provide information about the elemental compositions of core@shell and hollow nanoparticles. Copper atoms (red colour) located in the inner part of the Cu1.94S@Rh2S3 nanocrystal are rarely seen in the inner wall of the hollow Rh2S3 nanoparticle. The overall position of rhodium atoms (green colour) is not altered by the etching process. The removal of the Cu1.94S core by acid etching is also indicated by the X-ray diffraction (XRD) patterns taken before and after etching shown in Fig. S2 (ESI†); the XRD signals corresponding to Cu1.94S are selectively diminished after the core etching of Cu1.94S@Rh2S3.

In order to better understand the formation process of Cu1.94S@Rh2S3 nanoprism, the reaction intermediates obtained after 10 000 cycling of long-term durability tests, suggesting excellent structural integrity under strongly acidic conditions.

Scheme 1  Schematic Illustration of the formation process of facet-controlled hollow rhodium sulphide nanoparticles.

Fig. 1  (a) TEM image of Rh2S3 hollow nanoprisms. (b and c) HRTEM images of hexagonal face of a nanop prism and side of vertically standing nanoparticles, respectively; the enlarged views of image in the red square and the corresponding FFT patterns are shown below each figure. (d and e) STEM and elemental mapping images of a hexagonal face of a nanop prism and side of a vertically standing nanoparticle, respectively.
We controlled the size and thickness of the nanocrystals to investigate the relationship between the morphology and catalytic activity. The void volume and thickness of the hollow nanocatalyst have been considered as crucial factors in catalytic activity. Three hollow nanoprisms, namely, Rh$_2$S$_3$ _ThinHNP, Rh$_2$S$_3$ _MedHNP, and Rh$_2$S$_3$ _ThickHNP, were prepared by using 8:1, 8:2, 8:4 ratios of CuSCN:Rh(acac)$_3$, respectively, and their TEM images with corresponding FFT patterns and size analyses are shown in Fig. 2 (see Table S1 (ESI†) for synthetic details). At a constant CuSCN concentration, lower Rh(acac)$_3$ concentration yielded thinner nanoprisms with a higher aspect ratio and smaller void volume; the aspect ratios of the three samples are 10.7, 7.9, and 4.9, respectively. Interestingly, the cavity size was found to correlate with the shell thickness of the Rh$_2$S$_3$ nanocrystal, which was obtained by varying the ratio of CuSCN and Rh(acac)$_3$ precursors. The average thicknesses of the cavity were found to be 0.79 nm, 2.2 nm, and 3.7 nm for Rh$_2$S$_3$ _ThinHNP, Rh$_2$S$_3$ _MedHNP, and Rh$_2$S$_3$ _ThickHNP, respectively.

Next, we investigated the electrocatalytic activities of size- and thickness-controlled hollow Rh$_2$S$_3$ nanoprisms for the HER. For this purpose, the three Rh$_2$S$_3$ nanoprisms were supported on carbon black (Vulcan carbon) and nominal loading of Rh$_2$S$_3$ HNP was 13 wt%. For comparison, the electrocatalytic activities of C$_{1.94}$S@Rh$_2$S$_3$ _ThickNP/C, 20 wt% Pt/C, and carbon black were also investigated. The electrocatalytic activities were measured using a three-electrode electrochemical cell with Ag/AgCl and a graphite rod as the reference electrode and the counter electrode, respectively. All polarization curves were presented after the correction for Ohmic potential drop (iR) loss arising from solution resistance and normalization of the current with the geometric surface area of the electrode (0.1257 cm$^2$). As shown in HER polarization curves (Fig. 3a), the Rh$_2$S$_3$ _ThickHNP/C catalyst showed the best HER activity among the compared samples. To drive a current density of $-10$ mA cm$^{-2}$, the Rh$_2$S$_3$ _ThinHNP/C showed an overpotential of 122 mV, whereas the C$_{1.94}$S@Rh$_2$S$_3$ _ThickNP/C, Rh$_2$S$_3$ _MedHNP/C and Rh$_2$S$_3$ _ThinHNP/C required larger overpotentials of 175 mV, 175 mV, and 300 mV, respectively. The importance of hollow morphology was further proved by the superior HER performance of Rh$_2$S$_3$ _ThickHNP/C compared to that of C$_{1.94}$S@Rh$_2$S$_3$ _ThickNP/C (Fig. 3a). The non-etched sample (C$_{1.94}$S@Rh$_2$S$_3$ _ThickNP/C) showed considerably high HER activity, which is similar to that of Rh$_2$S$_3$ _MedHNP/C, and even higher than that of Rh$_2$S$_3$ _ThinHNP/C samples. This result clearly suggests that the active surface sites in the hollow Rh$_2$S$_3$ nanostructures originate from not only inside but also outside the hollow structure. In addition, the unusual shape of the LSV curve for Rh$_2$S$_3$ _ThinHNP/C could be attributed to the limited mass transport due to the relatively smaller void volume of Rh$_2$S$_3$ _ThinHNP compared to other hollow Rh$_2$S$_3$ NPs. The results emphasize the importance of a relatively wide cavity for facilitating mass transport along with the enhanced catalytic active sites. We note that while the above activity comparison among a series of Rh$_2$S$_3$/C catalysts has device-level relevance, more fundamental insights can be obtained by quantifying the activity per single
active site, which could be accomplished with more well-defined model catalysts such as Rh₂S₃-based single crystals.

To investigate the reaction kinetics during the HER, Tafel slopes were extracted from the linear portion of Tafel plots, derived from LSV polarization curves (Fig. 3b). The Tafel slope of 20 wt% Pt/C was 30 mV s⁻¹, indicating a Volmer–Tafel mechanism.²⁴ The Tafel slopes of Rh₂S₃_ThickHNP/C, Rh₂S₃_MedHNP/C, and Rh₂S₃_ThinHNP/C were approximately 44, 49, and 65 mV dec⁻¹, respectively. The relatively small Tafel slope of Rh₂S₃_ThickHNP/C indicated faster kinetics during the HER. All the Tafel slopes of 44–65 mV dec⁻¹ for Rh₂S₃/C may suggest the Volmer–Heyrovsky HER mechanism.⁶⁶ The Tafel slope of 44 mV dec⁻¹ for Rh₂S₃/C_ThickHNP is smaller than those of most metal sulphide-based HER catalysts. We extensively compared the HER activity and kinetics of the Rh₂S₃_ThickHNP/C catalyst with previously reported metal sulphide-based HER catalysts. Fig. 4 and Table 1 present the overpotentials required to drive −10 mA cm⁻² and the Tafel slopes for the HER of representative metal sulphide catalysts.

It is clear that the HER performance of the Rh₂S₃_ThickHNP/C catalyst is one of the best among the compared HER catalysts in terms of overpotential and the Tafel slope (Fig. 4 and Table 1). In addition, we explored the catalyst loading effect toward HER. The HER performance was enhanced with increasing catalyst loading (Fig. S4, ESI†). Rh₂S₃_ThickHNP/C with a catalyst loading of 918 mg cm⁻² reached a geometric current density of −10 mA cm⁻² at overpotential of only 88 mV, which is the highest performance among the sulfide-based HER catalysts (Fig. 4 and Table 1).

We next examined the long-term stability of Rh₂S₃_ThickHNP/C by conducting consecutive potential cycles between 0.1 and −0.3 V (vs. RHE) at a sweep rate of 50 mV s⁻¹. Fig. 3c shows polarization curves recorded before and after 10 000 potential cycles. Interestingly, after 10 000 CV cycles, the overpotential to reach a current density of −10 mA cm⁻² was considerably reduced from 137 mV to 117 mV (data were presented without iR compensation). To the best of our knowledge, such enhancement of catalytic activity after the cycling test has not been reported in previous sulphide-based HER catalysts (Fig. 3c and Table 1). The potential cycles further removed the inactive Cu impurities from the hollow Rh₂S₃ nanoparticles, which would increase the number of active Rh-based catalytic sites. The Cu leaching was confirmed by measuring the content of Cu in the electrolyte before and after 10 000 potential cycles using inductively coupled plasma optical emission spectrometry (ICP-OES) (Table S2, ESI†). TEM images after potential cycles revealed that the hollow structure of Rh₂S₃ nanoparticles is well preserved and the nanoprisms are uniformly distributed on the carbon support without agglomeration (Fig. S5 ESI†). Inspired by the finding that residual Cu impurities could block the active catalytic sites, we prepared Rh₂S₃_ThickHNP/C with an increased etching time of 24 h. Even though the amount of Cu was reduced to one-third (from 1.50 wt% to 0.53 wt%, determined via ICP-OES), the HER activity was inferior to that of Rh₂S₃_ThickHNP/C with 3 h etching time (Fig. S6, ESI†). The 24 h etching time could destroy the hollow morphology, affecting the HER performance. Thus, we conclude that the relatively mild electrochemical leaching of remnant Cu was advantageous for preserving the hollow morphology, which appears to be a decisive factor determining the HER performance.

**Conclusions**

In conclusion, we have developed a highly active Rh₂S₃-based nanocatalyst toward HER, which is very robust under strongly acidic operation conditions. The facet-controlled hollow nanostructure of Rh₂S₃ could be conveniently obtained by thermal co-decomposition of Rh(acac)₃ and CuSCN, and subsequent removal the Cu₁.₉₄S core from the core–shell Cu₁.₉₄@Rh₂S₃ hexagonal prism by acid etching. The hollow Rh₂S₃ nanoprisms...

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**Fig. 4** HER activity comparison graph showing the Tafel slope (mV dec⁻¹) with overpotential (mV vs. RHE) to reach a current density of −10 mA cm⁻².
with catalytically highly active sites give rise to excellent catalytic activity and structural robustness for the HER. We believe that the synthetic strategy of this study can be applied to prepare other catalytically useful hollow nanostructures and relevant synthetic endeavour is currently under way.

**Experimental section**

**Synthesis**

In a typical synthesis of hollow Rh$_2$S$_3$ nanoprims, a slurry of CuSCN and Rh(acac)$_2$ in oleylamine was prepared in a 100 mL Schlenk tube. After being placed under vacuum at 100 °C for 10 min, the reaction mixture was charged with 1 atm Ar gas. Then the Schlenk tube was placed in a hot oil bath, which was preheated to 240 °C. After heating at the same temperature for 30 min, the reaction mixture was cooled down to room temperature, was washed several times with toluene and methanol, followed by centrifugal separation to give Cu$_{13.9}$S@Rh$_2$S$_3$ nanoprims. The nanoprims were then etched in a solution containing 1 mL of HCl, 3 mL of EtOH, and 3 mL of toluene for 3 hours with a magnetic stirring to give hollow Rh$_2$S$_3$ nanoprims. For the electrocatalytic measurement, carbon black Vulcan XC-72R powder was put into a 70 mL vial with 20 mL of hexane, and were sonicated for 10 minutes. After 10 minutes, the slurry with nanoparticles was poured into the 70 mL vial containing carbon black, and the combined slurry was sonicated for additional 3 minutes. The resultant slurry with nanoparticles loaded on carbon black was transferred to a 50 mL conical tube, and 20 mL of hexane was added to the slurry. After this procedure, the nanoparticles loaded on carbon black were separated by centrifugation and then dried in an oven for 24 hours.

**Material characterization**

Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) were performed on a TECNAI G2 20 S-Twin operated at 200 kV and TECNAI G2 F30 operated at 300 kV. All scanning transmission electron microscopy (STEM) images and compositional maps were acquired with the use of HAADF-STEM and an energy dispersive X-ray spectrometer attached in the TECNAI G2 F30 ST. In order to visualize elemental map from our nanoparticles, the electron probe was set <0.3 nm and the camera length of STEM was selected at 120 mm. The elemental maps were digitized by 25 × 25 pixels for 25 nm by 25 nm area and the collection time of each pixel was 0.9 second. X-ray diffraction (XRD) patterns were collected using a Rigaku Ultima III diffractometer system with a graphite-monochromatized Cu-Kα radiation at 40 kV and 40 mA. X-ray photoelectron spectroscopy was performed on a UIVAC X-Tools. The detector angle was set at 45° and the incidence angle of X-ray was set at 90°.

**Electrochemical characterization**

All electrochemical measurements were performed on an IviumStat electrochemical analyzer at room temperature under atmospheric conditions.

### Table 1  HER activity comparison table showing the Tafel slope (mV dec$^{-1}$) with overpotential (mV)

<table>
<thead>
<tr>
<th>Class of catalyst</th>
<th>Catalyst</th>
<th>Loading</th>
<th>Overpotential (mV vs. RHE)@−10 mA cm$^{-2}$</th>
<th>Tafel slope (mV dec$^{-1}$)</th>
<th>Ref.</th>
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</thead>
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<tr>
<td>MoS$_2$-based catalysts</td>
<td>ETIE MoS$_2$</td>
<td>280 μg cm$^{-2}$</td>
<td>149</td>
<td>49</td>
<td>13</td>
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<tr>
<td></td>
<td>MoS$_2$</td>
<td>—</td>
<td>161</td>
<td>39</td>
<td>14</td>
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<tr>
<td></td>
<td>Li-MoS$_2$/CF</td>
<td>3.4 to 3.9 mg cm$^{-2}$</td>
<td>118</td>
<td>62</td>
<td>15</td>
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<tr>
<td></td>
<td>MoS$_2$/NCNT</td>
<td>—</td>
<td>110$^a$</td>
<td>40$^a$</td>
<td>16</td>
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<tr>
<td></td>
<td>[MoS$_2$]$_2$</td>
<td>100 μg cm$^{-2}$</td>
<td>173</td>
<td>40</td>
<td>17</td>
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<td></td>
<td>1T-MoS$_2$</td>
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<td>43</td>
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<td></td>
<td>MoS$_2$@OMC</td>
<td>300 μg cm$^{-2}$</td>
<td>182</td>
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<td>Defect rich MoS$_2$</td>
<td>285 μg cm$^{-2}$</td>
<td>191$^a$</td>
<td>50$^a$</td>
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<td></td>
<td>Oxygen-MoS$_2$</td>
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<td>DG-MoS$_2$</td>
<td>60 μg cm$^{-2}$</td>
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<td>Cu$_x$MoS$_2$</td>
<td>41.6 μg cm$^{-2}$</td>
<td>329$^a$</td>
<td>95$^a$</td>
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<td></td>
<td>MoS$_2$/rGO</td>
<td>280 μg cm$^{-2}$</td>
<td>150</td>
<td>41</td>
<td>24</td>
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<td>350 μg cm$^{-2}$</td>
<td>158$^a$</td>
<td>48$^a$</td>
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<td>WS$_2$ Nanoribbons</td>
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<td>Metallic WS$_2$ nanosheets</td>
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<td>70</td>
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<td>W$_2$O$_4$@WS$_2$ NRs</td>
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<td>319$^a$</td>
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<td></td>
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<td>400 μg cm$^{-2}$</td>
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<td>58$^a$</td>
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<tr>
<td>Fe, Co, Ni sulfide based catalysts</td>
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<td>&gt;200</td>
<td>48.8</td>
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$^a$ HER activity parameter reported without iR-correction.
pressure using a three-electrode electrochemical cell. A graphite rod and Ag/AgCl (in saturated KCl solution) were used as the counter electrode and the reference electrode, respectively. The Ag/AgCl reference electrode was calibrated with respect to the reversible hydrogen electrode (RHE) before every use. For the calibration, a hydrogen reference electrode (Hydroflex®, Gaskatel) and the Ag/AgCl electrode were immersed in 0.5 M H2SO4 for 30 min. The open circuit voltage (OCV) was recorded, resulting in E(RHE) = E(Ag/AgCl) – OCV. All potentials in this report were presented in the RHE scale. For electrochemical measurement, a rotating ring-disk electrode (RRDE) containing a glassy carbon (GC) as a central disk (4 mm diameter, 0.126 cm2 area) was used as the working electrode. The RRDE was polished with a 1.0 µm alumina suspension, and then with a 0.3 µm suspension to generate a mirror finish before use. Catalyst inks were prepared by mixing 5 mg of the catalyst with 40 µL of Nafion (5 wt% in isopropanol, Sigma-Aldrich) in a solution of 750 µL of DI water, 250 µL of EtOH (99.9%), and the mixture was sonicated for 30 min to produce homogeneous slurry. Afterwards, 4 µL of the catalyst ink was dropped onto the glassy carbon electrode, and dried at 70 °C for 5 min. The resulting catalyst loading on GC was 153 µg cm−2. Before electrochemical measurements, the 0.5 M H2SO4 electrolyte was bubbled with N2 for 20 min followed by conducting cyclic voltammetry (CV) for electrochemical cleaning; this consisted of 20 repetitions in a potential range of 0.01 to 1.2 V (vs. RHE) at a scan rate of 50 mV s−1. In the case for 20 wt% Pt/C (Johnson-Matthey, HiSPEC-3000), electrochemical cleaning was conducted in a potential range of 0.05 V to 1.2 V (vs. RHE) at a scan rate of 500 mV s−1, followed by three CVs at a scan rate of 50 mV s−1. After the electrochemical cleaning by CV, the electrochemical impedance spectroscopy (EIS) was conducted in a frequency range of 100 kHz to 0.01 Hz at an overpotential of 100 mV. The linear sweep voltammetry (LSV) curves in this paper were plotted after compensating the ohmic drop with the Rs value obtained from the EIS measurements. Linear sweep voltammetry (LSV) for the hydrogen evolution reaction (HER) was conducted from 0.1 V to −0.4 V (vs. RHE) at a scan rate of 2 mV s−1 with a rotating speed of 1500 rpm in 0.5 M H2SO4. A long-term cycling test was conducted by performing consecutive cyclic voltammetry (CV) measurements between 0.1 and −0.3 V (vs. RHE) at a sweep rate of 50 mV s−1 with a rotation speed of 1500 rpm. LSV polarization curves were recorded before and after the cycling test without iR-correction.

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Notes and references
