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Electronic Supporting Information

Ultrathin Rh nanosheets as highly efficient bifunctional electrocatalyst for the isopropanol-assisted overall water splitting

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Experimental section

Reagents and chemicals

Rhodium (III) chloride hydrate ($RhCl_3 \cdot 3H_2O$), potassium hydroxide (KOH), potassium ferricyanide ($K_3Fe(CN)_6$), and formaldehyde (HCHO) were purchased from Adamas Reagent Co., Ltd.. **The** commercial Pt nanocrystals (Pt-NCs) was purchased from Johnson Matthey Corporation.

Preparation of Rh-NSs

In a typical synthesis, the 3 mL of mixture solution containing 0.15 M $RhCl_3$ and 0.15 M $K_3Fe(CN)_6$ was heated at 80 ^oC for 8 h, which induced the generation of jelly-like $RhCl_3$-$K_3Fe(CN)_6$ cyanogel. After cooling, 2.0 mL of HCHO was added in the $RhCl_3$-$K_2Fe(CN)_6$ cyanogel. Then, the mixture was heated at 200 ^oC for 6 h, which induced the generation of Rh-NNs. After reaction, Rh-NSs were washed with 0.01 M HCl solution and water, and the dried at 60 °C for 8 h.

Electrochemical measurements

Various electrochemical measurements, such as CV, LSV, EIS, and chronopotentiometry, tests, were performed on CHI-660 electrochemical analyser at 30 °C. In a three-electrode cell, carbon rod, the saturated calomel electrode, catalyst-modified glassy carbon electrode were used as the auxiliary electrode, reference electrode, working electrode, respectively. The catalyst ink-transfer method was used to prepare the working electrode. The catalyst ink was got ready by dispersing 2 mg of the catalyst in 1.0 mL of water. The 4 μL of the catalyst ink was loaded onto the electrode surface and dried at room temperature. Then, Then, 4 μL of Nafion solution (0.05 wt%) was coated on the electrode surface and dried at room temperature. The metal loading density on working electrode was 0.11mg cm^{-2}.

Physical characterization

Transmission electron microscopy (TEM), high-resolution TEM (HRTEM), energy-dispersive X-ray (EDX) maps, and selected area electron diffraction (SAED) were carried out with a TECNAI G2 F20 instrument. Scanning electron microscopy (SEM) and EDX analysis were conducted with an SU-8020 instrument. N2 adsorption/desorption isotherm test was performed on a Micro-meritics ASAP 2020

HD88 physical adsorption instrument. X-ray diffraction (XRD) were performed on a DX-2700 power X-ray diffractometer. X-ray photoelectron spectroscopy (XPS) was conducted on an AXIS ULTRA spectrometer, and the binding energy was calibrated with C 1s peak at 284.6 eV. Atomic force microscopy (AFM) was carried out with a Dimension Icon instrument.

Figures and captions

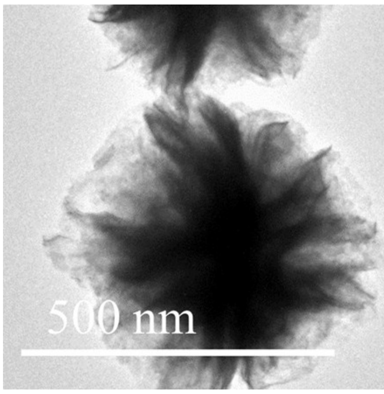

Fig. S1 TEM image of Rh-NSs after chronoamperometry test.

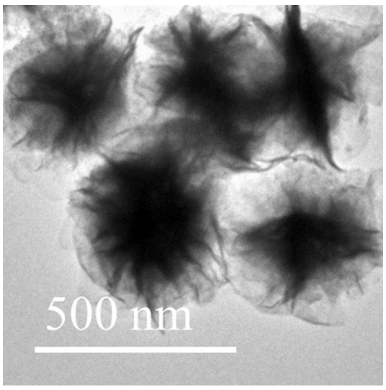

Fig. S2 TEM image of Rh-NSs after chronoamperometry test.

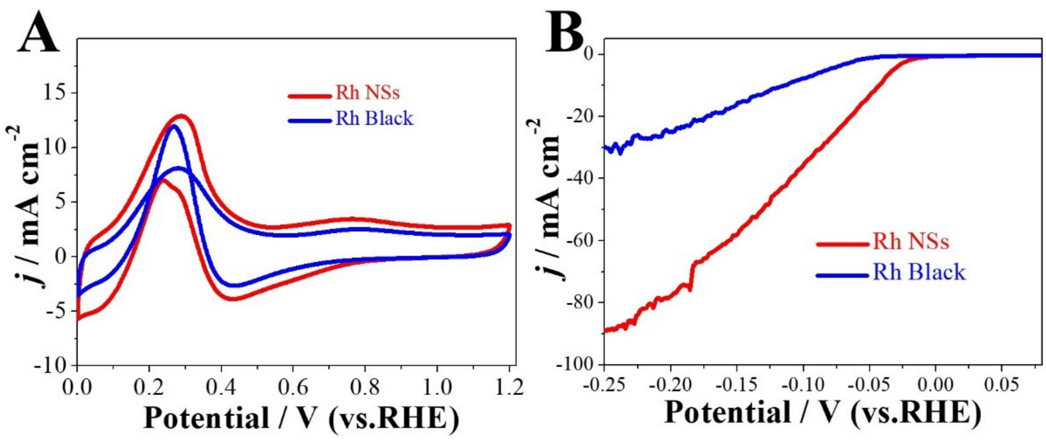

Fig. S3 (A) CV curves of Rh-NSs and Rh black in Ar-saturated 1.0 M KOH solution with 1.0 isopropanol at 50 mV s^{-1}. (B) LSV polarization curves of Rh-NSs and Rh black in Ar-saturated 1.0 M KOH solution at 5 mV s^{-1}.

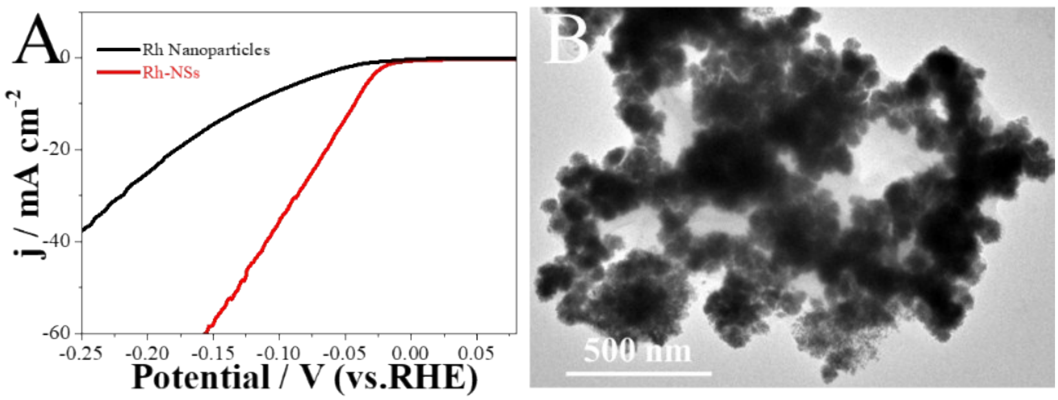

Fig. S4 (A) LSV polarization curves of Rh-NSs and spherical Rh nanoparticles in Ar-saturated 1.0 M KOH solution. (B) TEM image of spherical Rh nanoparticles. Herein, spherical Rh nanoparticles was synthesized by replacing $RhCl_3$-$K_3Fe(CN)_6$ cyanogel with $RhCl_3$ solution as the reaction precursor under same experimental conditions.

Table S1. HER activity of various precious metal based eleectrocatalysts in KOH solution.

Catalysts	Electrolyte	η_{10} value	Ref. (year)
Rh-NSs	1 M KOH	43 mV	This work
Pd nanonetwork	1 M KOH	110 mV	2017[1]
Mo_2C@NC@Pt nanospheres	1 M KOH	47 mV	2019[2]
$Ir_{0.80}Ru_{0.20}O_y$	1 M NaOH	ca. 45 mV	2017[3]
PtO_aPdO_bNPs@$Ti_3C_2T_x$	0.1 M KOH	57 mV	2018[4]
Pd@Ru core@shell nanorods	1 M KOH	30 mV	2018[5]
Modified Pt(111) by $Ni(OH)_2$	0.1 M NaOH	88 mV	2019[6]
$NiCo_2S_4$/Pd heterostructure	1 M KOH	83 mV	2018[7]
Pt/NiO@Ni/NF nanocomposite	1 M KOH	34 mV	2018[8]
Pt−$Co(OH)_2$ nanosheet	1 M KOH	32 mV	2017[9]
Rh nanocrystal at carbon nanotubes	1 M KOH	48 mV	2018[10]
Ultrafine Pt nanoparticles at CoS_2 nanosheet	1 M KOH	24 mV	2018[11]
Au doping in Co-Ni hydroxide	1 M KOH	35 mV	2018[12]
Ru nanoparticles on nitrogen-doped GnP	1 M KOH	22 mV	2018[13]
Pt-Ni anisotropic superstructures	1 M KOH	27.7 mV	2018[14]
Ultrathin Pt/Ni alloy nanowires	0.1 M KOH	38 mV	2018[15]
Palladium phosphide	1 M KOH	35.4 mV	2018[16]
N,P dual-doped carbon-encapsulated ruthenium diphosphide nanoparticle	1 M KOH	52 mV	2017[17]
Ru nanodendrites	1 M KOH	43.3 mV	2018[18]
Ru-doped Ni-Co bimetal phosphides	1 M KOH	52 mV	2017[19]
Fe–Pt mesoporous films	1 M KOH	74 mV	2018[20]
Pt nanostructure at N-Doped carbon	0.5 M KOH	51 mV	2018[21]
Pt nanoparticles at 2D-$Ni(OH)_2$ nanosheets	0.1 M KOH	ca. 118 mV	2018[22]
Pristine Ru-based electrode	0.1 M KOH	150 mV	2019[23]
$Ni(OH)_2$–PtO_2 hybrid nanosheet array	1 M KOH	100 mV	2018[24]
3D nanoporous Ag@Pd core@shell hybrids	1 M KOH	23.8 mV	2018[25]
Open hollow Co–Pt bimetallic nanoclusters	1 M KOH	50 mV	2018[26]
Pt nanoparticles at NiFe hydroxide	1 M KOH	101 mV	2017[27]
Pd nanoparticles on TiO_2 nanotube	1 M $HClO_4$	38 mV	2018[28]
Pt-Mn nanocubes on $Ni(OH)_2$ nanosheets	0.1 M NaOH	ca. 100 mV	2018[29]
Rh tetrahedron	1 M KOH	43 mV	2017[30]

Rh concave tetrahedra	1 M KOH	ca. 75 mV	2017[30]
Single-atom Pt_1 onto $Fe-N_4$ center	1 M KOH	ca.110 mV	2018[31]
PtCo alloy at Co nanowire array	1 M KOH	28 mV	2018[32]
Pt-decorated Ni_3N nanosheets	1 M KOH	ca.50 mV	2017[33]
Octahedral Pt-Co alloy nanocrystals	0.1 M KOH	ca.50 mV	2017[34]

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