Electronic Supplementary Information

Formation of Cu@RhRu core-shell concave nanooctahedron via Ru-assisted extraction of Rh from the Cu matrix and its excellent electrocatalytic activity toward oxygen evolution reaction

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Material Characterizations

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 energy dispersive X-ray spectrometer attached in the TECNAI G2 F30 ST. In order to visualize elemental map from our nanoparticle, the electron probe was set < 0.3nm and the camera length of STEM was selected at 120mm. The elemental maps were digitized by 25x25 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 with a Rigaku Ultima III diffractometer system using a graphite-monochromatized Cu-K α radiation at 40 kV and 40 mA. X-ray photoelectron spectroscopy were performed on a UIVAC X-Tool. The detector angle was set at 45° and incidence angle of Xray was set at 90°. The contents of Cu, Rh, and Ru of the reaction intermediate at 5 min were also analyzed by using inductively coupled plasma atomic emission spectrophotometer (ICP AES, JY Ultima2C) at Korea Basic Science Institute in Seoul; sample was analyzed three times and averaged.

Experimental Section

Preparation of Cu@RhRu core-shell concave nanooctahedron

A slurry of Ru(acac)₃ (0.015 mmol, STREM Chemicals, 99 %), Rh(acac)₃ (0.005 mmol, STREM Chemicals, 99.9 %), Cu(OAc)₂ (0.020 mmol, Aldrich, 98 %), and CTAB (cetyltrimethylammonium bromide)(0.020 mmol, Aldrich, 99 %) in oleylamine (15 mmol, Aldrich, 70 %) was prepared in a 100 mL Schlenck tube. After placing the reaction mixture under vacuum at 25 °C for 10 min, the reaction mixture was charged with 1 atm CO gas. Then the Schlenk tube was directly placed in a hot oil bath, which was preheated to 270 °C. After heating at the same temperature for 20 min, the reaction mixture was

cooled down to room temperature. The reaction mixture, after being cooled down to room temperature and being added 20 mL toluene and 10 mL methanol, was centrifuged at 3500 rpm for 10 min. The resulting precipitates, with added methanol/toluene (v/v = 1/2 mL), were further purified by centrifugation at 3500 rpm for 5 min.

Preparation of CuRh nanoparticles

A slurry of Cu(OAc)₂ (0.020 mmol, Aldrich, 98 %), Rh(acac)₃ (0.005 mmol, STREM Chemicals, 99.9 %), and CTAB (cetyltrimethylammonium bromide)(0.020 mmol, Aldrich, 99 %) in oleylamine (15 mmol, Aldrich, 70 %) was prepared in a 100 mL Schlenck tube. After placing the reaction mixture under vacuum at 25 °C for 10 min, the reaction mixture was charged with 1 atm CO gas. Then the Schlenk tube was directly placed in a hot oil bath, which was preheated to 270 °C. After heating at the temperature for 20 min, the reaction mixture was cooled down to room temperature and being added 20 mL toluene and 10 mL methanol, was centrifuged at 3500 rpm for 10 min. The resulting precipitates, with added methanol/toluene (v/v = 1/2 mL), were further purified by centrifugation at 3500 rpm for 5 min.

Preparation of Rh nanoparticles

A slurry of Rh(acac)₃ (0.020 mmol, STREM Chemicals, 99.9 %) in oleylamine (15 mmol, Aldrich, 70 %) was prepared in a 100 mL Schlenck tube. After placing the reaction mixture under vacuum at 25 °C for 10 min, the reaction mixture was charged with 1 atm CO gas. Then the Schlenk tube was directly placed in a hot oil bath, which was preheated to 270 °C. After heating at the temperature for 20 min, the reaction mixture was cooled down to room temperature and being added 20 mL toluene and 10 mL methanol, was centrifuged at 3500 rpm for 10 min. The resulting precipitates, with added methanol/toluene (v/v = 1/2 mL), were further purified by centrifugation at 3500 rpm for 5 min.

Electrochemical measurement of Cu@RhRu core-shell concave nanooctahedron

Indium-tin oxide (ITO) electrodes were obtained from Corning (Daegu, Korea) and pretreated by dipping in 1 M HCl for 10 min. To prepare Rh nanoparticle-, hollow Ru cage nanoparticle-,¹ and Cu@RhRu nanocrystal-modified electrodes, 70 µL of an ethanol solution containing 100 µg/mL each nanoparticle was dropped onto ITO electrodes (1 cm × 2 cm). Afterward, the electrodes were dried at 80 °C for 10 min. Electrochemical measurements were carried out using CHI 617 (CH Instruments, Inc., Austin, TX, USA). A Teflon electrochemical cell was assembled with an ITO working electrode, an Ag/AgCl (3 M NaCl) reference electrode, and a Pt counter electrode. The exposed electrode area was 0.28 cm².



Fig. S1 Co-decomposition of Ru and Rh precursors (1:1 ratio) heated at a) 210 °C, b) 230 °C, c) 250 °C, and d) 270 °C in the absence of Cu precursor.



Fig. S2 Size distribution of 15.5 ± 1.2 nm Cu@RhRu core-shell octahedral nanocrystals.



Fig. S3 XRD pattern of Cu@RhRu core-shell concave nanooctahedron in Fig. 1. XRD analysis shows the *fcc* atomic structure of Cu, Rh and Ru.



Fig. S4 Elemental mapping analyses by energy dispersive X-ray spectroscopy of intermediates obtained at a) 5 min, b) 7 min, c) final product. d) Inductively coupled plasma atomic emission spectrophotometer (ICP AES) analysis for 5 min sample.



Fig. S5 Line scan elemental profile of the spherical and plate-like shaped RuRh nanoparticles from co-decomposition of Ru and Rh precursors in the absence of Cu precursor.



Fig. S6 a) High resolution TEM image of the RuRh nanoparticles in Fig. S5. b-c) HRTEM images and d-e) FFT patterns of two different nanostructures in a). The FFT patterns with zone axis of [001] are observed in region i), and zone axis of [111] is observed in region ii). This reveals a *hcp* atomic structure of RuRh nanoparticles for region i) and region ii).



Fig. S7 XRD pattern of spherical and plate-like nanostructures of RuRh nanoparticles in Fig. S5. This reveals *hcp* atomic structure of RuRh nanoparticles.



Fig. S8 CuRhRu NPs synthesized a) under Ar condition or b) under CO without CTAB.



Fig. S9 Co-decomposition of Cu and Rh precursors (4:1 ratio) and CTAB surfactant in the absence of Ru precursor.



Fig. S10 Line scan elemental profile of the CuRh nanoparticles. Alloy nanofeatures are shown clearly.



Fig. S11 X-ray photoelectron spectra (XPS) of Cu@RhRu core-shell concave nanooctahedron. Partial oxidation of Cu, Rh and Ru is observed. It is found that Cu and Rh in concave nanooctahedron exist as 31.8 % Cu(0), 34.9 % Cu(I) and 33.3 % Cu(II), 91.8 % Rh(0) and 8.2 % Rh(III). Ru was found as 29.7 % Ru(0) and 70.3 % Ru(IV).

Element Peak Energy (eV)		Element Peak Energy (eV)		Element Peak Energy (eV)	
Cu(0) 2p _{3/2}	932.63	Rh(0) 3d _{c/0}	307 20	Ru(0) 3d	280 10
Cu(I) 2p _{3/2}	932.18	nn(0) 00 _{5/2}	001.20	114(0) 045/2	200.10
Cu(II) 2p _{3/2}	933.76	Rh(III) 3d _{5/2}	308.30	Ru(IV) 3d _{5/2}	280.90

Fig. S12 Reference binding energies (BE) of the Cu 2p, Rh 3d and Ru 3d used for analyzing XPS spectra.^{1,2}



Fig. S13 Synthesized Rh nanoparticles used for OER activity study in Fig. 4.

Reference

- 1 D. Yoon, S. Park, J. Park, J. Kim, H. Baik, H. Yang and K. Lee, *Nanoscale*, 2014, 6, 12397.
- 2 Y. Zhang, M. E. Grass, S. E. Habas, F. Tao, T. Zhang, P. Yang and G. A. Somorjai, J. Phys. Chem. C, 2007, 111, 12243.