Cactus like $Cu_{2-x}S@IrS_y@IrRu$ alloy nanoparticles as highly efficient bifunctional electrocatalysts for overall water splitting in acidic media

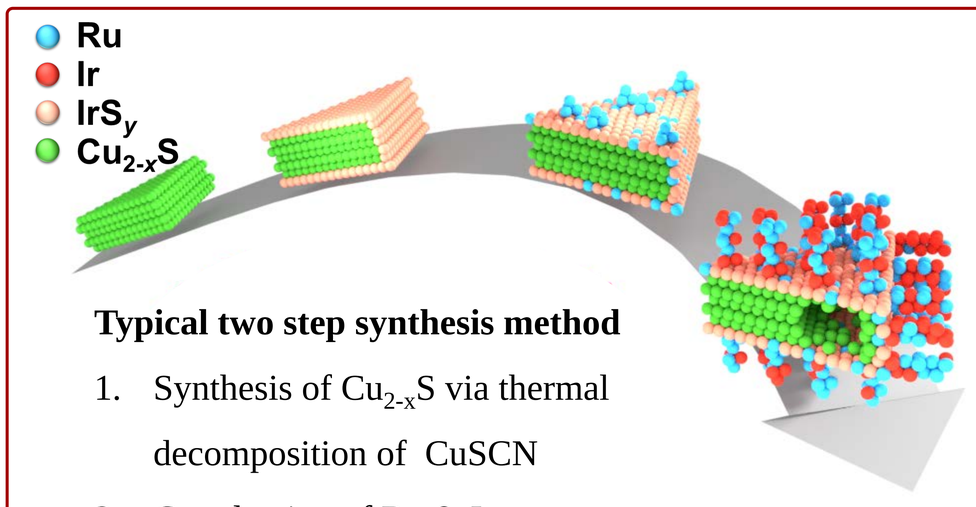
Jinwhan Joo[1,2], Haneul Jin[1,2], Kwangyeol Lee[1,2*]

[1]Center for Molecular Spectroscopy and Dynamics, Institute for Basic Science (IBS), Seoul 02841, Korea
[2]Department of Chemistry, Korea University, Seoul 02841, Korea

Abstract

Bifunctional electrocatalysts for the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER) is mandatory for clean and sustainable alternative energy sources. To improve the efficiency of the overall water splitting, highly efficient and stable bifunctional electrocatalysts in acidic media is vital for polymer electrolyte membrane (PEM) electrolyzers. Herein, we synthesized cactus like $Cu_{2-x}S@IrS_y@IrRu$ (CIS@IrRu) alloy nanoparticles via template mediated method, which show highly efficient HER and OER electrocatalytic activity. Due to the dendritic structure and stable IrSy shell, the cactus like CIS@IrRu nanoparticles exhibit highly efficient HER and OER catalytic activity in acidic media. The CIS@IrRu nanoparticles show the Ir/Ru composition dependent electrocatalytic activity with best bifunctional performance at the Ir ratio to Ru is 1.00 to 1.07.

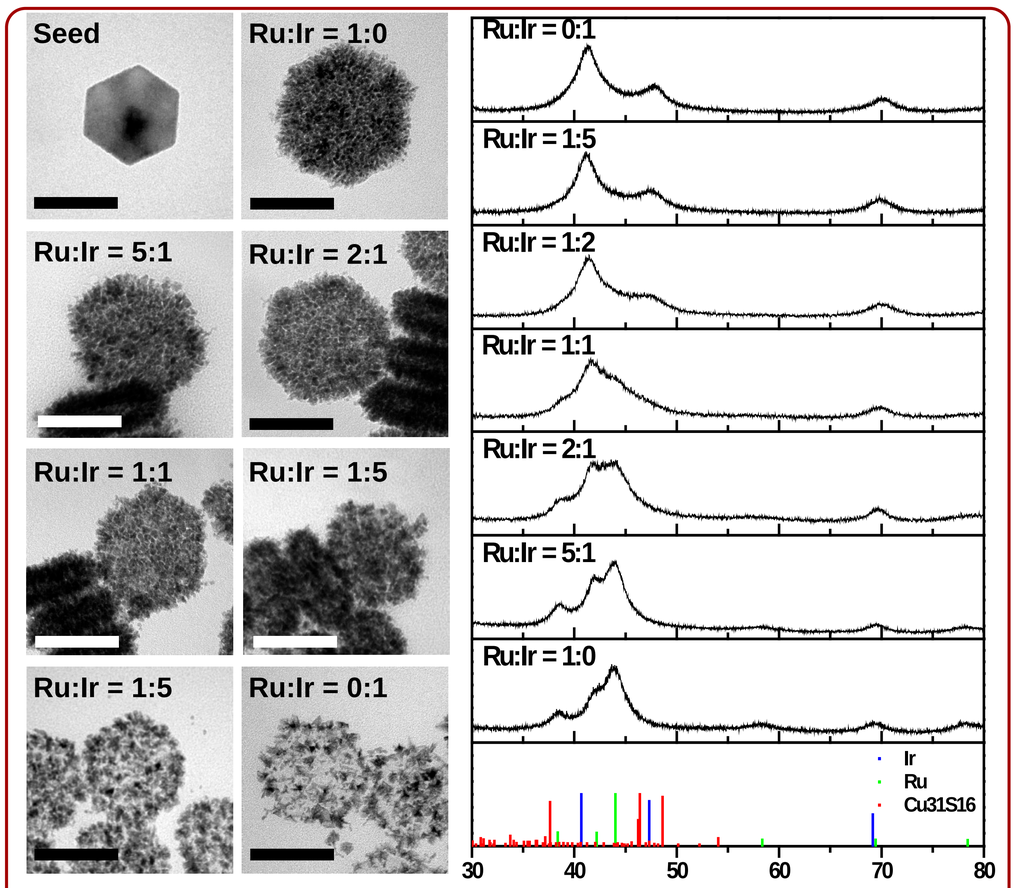
Schematic images of CIS@IrRu NPs



Typical two step synthesis method

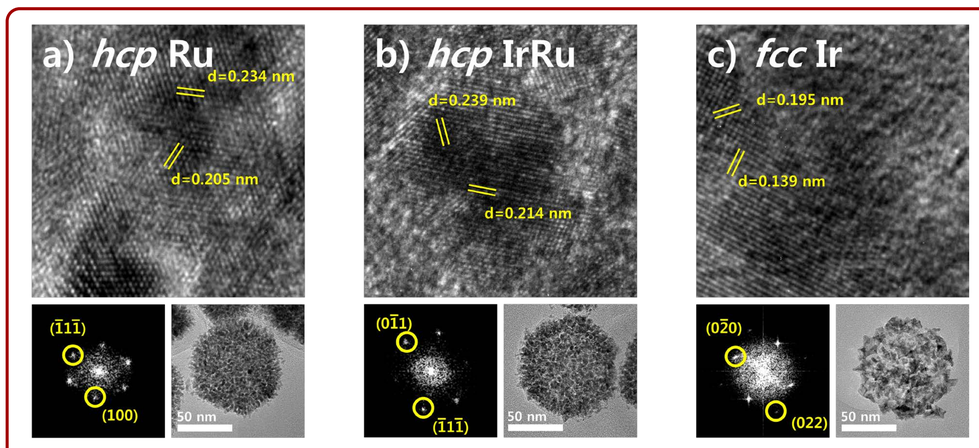
1. Synthesis of $Cu_{2-x}S$ via thermal decomposition of CuSCN
2. Coreduction of Ru & Ir precursors

Compositional analysis



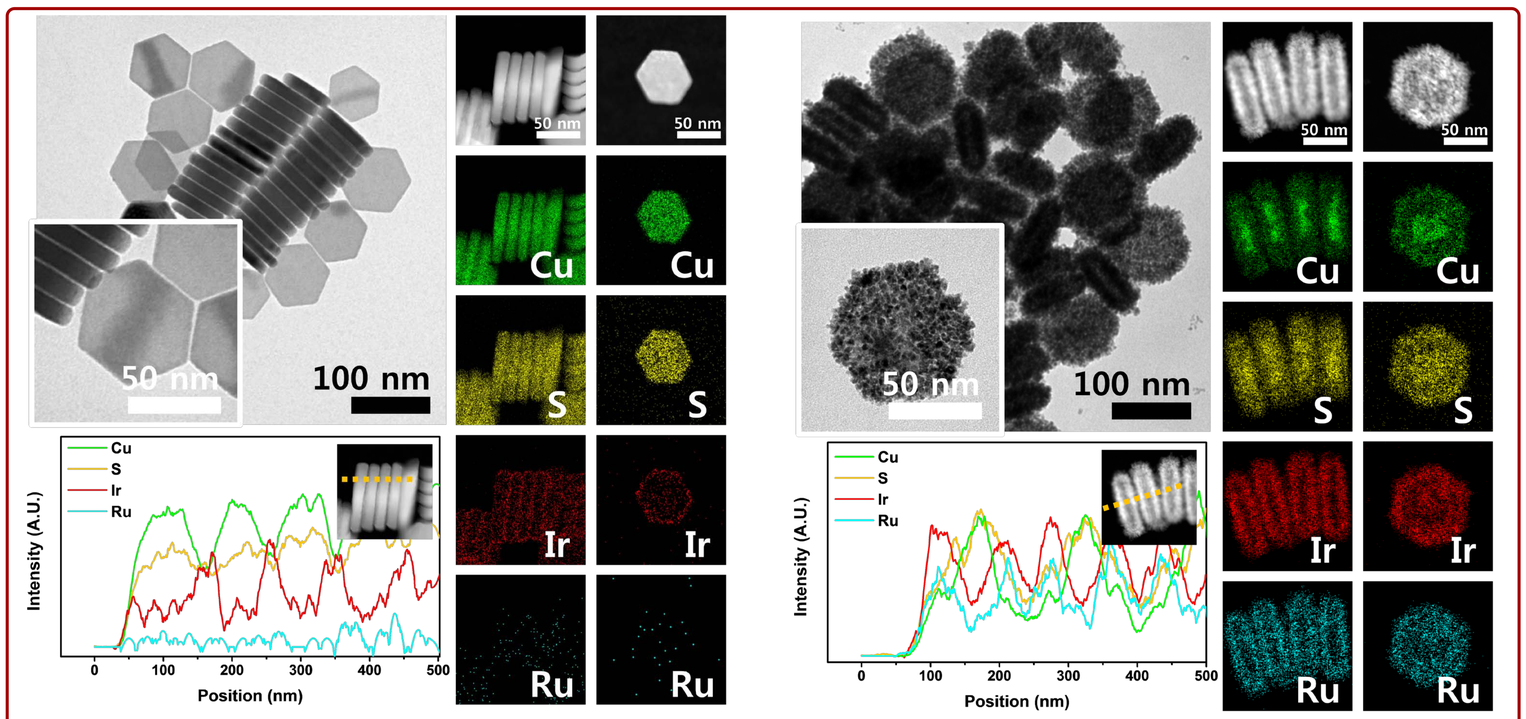
The TEM and XRD analysis are performed for compositional trend. Ru rich samples show more prickly structure than Ir rich samples. Also XRD patterns shift from *hcp* metallic Ru to *fcc* metallic Ir as the ration of Ir to Ru increases. The scale bar is 50 nm.

HRTEM analysis



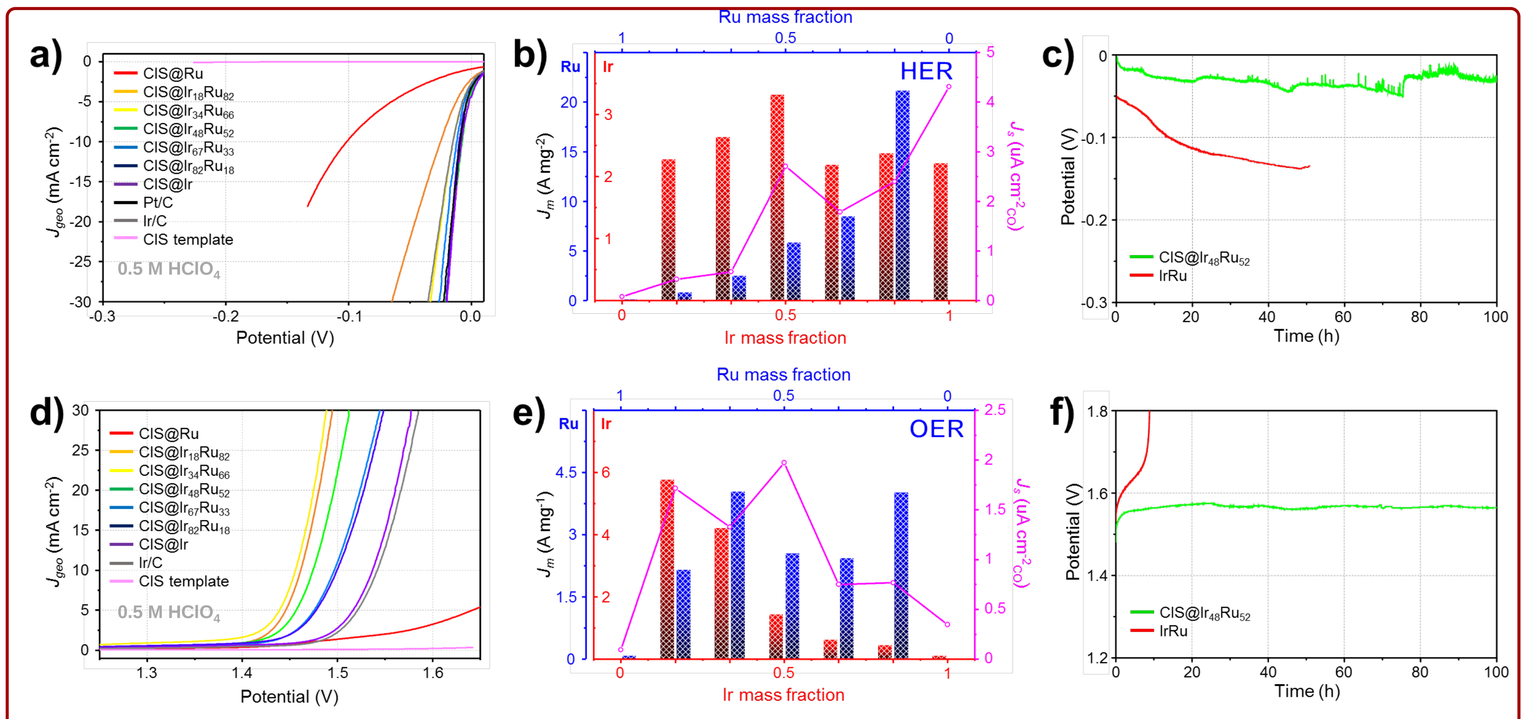
The HRTEM analysis are performed for compositional trend. CIS@Ru and $CIS@Ir_{48}Ru_{52}$ follow *hcp* crystal structure and CIS@Ir follow *fcc* structure. In addition, $CIS@Ir_{48}Ru_{52}$ has larger lattice distance compare to CIS@Ru, due to the alloying of Ir.

TEM and Elemental analysis of CIS and $CIS@Ir_{48}Ru_{52}$



The TEM images show the as-synthesized CIS template and $CIS@Ir_{48}Ru_{52}$ NPs. The $CIS@Ir_{48}Ru_{52}$ NPs are highly monodisperse with a width of 95.9 ± 3.7 nm, measured from the diagonal point to point, and a thickness of 36.2 ± 2.1 nm, which is significantly increased compare to CIS template. In addition, the elemental mapping and line profile of $CIS@Ir_{48}Ru_{52}$ NPs prove once again that $Cu_{2-x}S$ is remain at the core and complete alloy of Ir and Ru.

Electrocatalytic analysis of CIS@IrRu with various composition



(a,d) HER and OER Polarization curves of various $CIS@Ir_xRu_{1-x}$, commercial Pt/C, and Ir/C. **(b,e)** Comparison of mass activities in HER and OER by Ir (red) and Ru (blue) mass fractions at 20 mV and 250 mV of overpotential and current densities by ECSA (magenta). **(c,f)** Comparison of stabilities of $CIS@Ir_{48}Ru_{52}$ (green) and IrRu NPs (red) at 5 mA cm^{-2} of constant current.

The Ir/Ru surface alloy composition could be conveniently controlled by varying the ratio of Ir and Ru precursors, and more importantly, the catalytic performance of the CIS@IrRu alloy NPs could be fine-tuned by varying the Ir/Ru alloy composition.

Conclusion

In summary, we have used seed-mediated two step method to prepare cactus-like. By coreduction of different ratio of Ir to Ru precursors, we were able to change elemental composition and structure. The remained CIS seed is expected to enhance stability. According to the electrocatalytic analysis, the cactus-like CIS@IrRu NPs exhibits excellent electrocatalytic activity and stability toward both HER and OER in acidic electrolyte. This work was supported by the Institute for Basic Science (IBS-R023-D1), the National Research Foundation of Korea (NRF-2017R1A2B3005682)