Electronic Supplementary Information

Facet-controlled hollow Rh_2S_3 hexagonal nanoprisms as highly active and structurally robust catalysts toward hydrogen evolution reaction

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1. Supporting Tables S1-S2

Table S1. Synthetic conditions for morphology controlled nanocrystals shown in Fig. 2.

Sample	Cu(SCN)	$Rh(acac)_3$	oleylamine
ThinHNP	0.10 mmol	0.0125 mmol	10 mL (30 mmol)
MedHNP	0.10 mmol	0.0250 mmol	10 mL (30 mmol)
ThickHNP	0.10 mmol	0.0500 mmol	10 mL (30 mmol)

All samples were synthesized at 240 ^{0}C for 30 minutes. After synthesizing $Cu_{1.94}S@Rh_2S_3$ core-shell nanocrystals, the hollow Rh_2S_3 nanocrystals were prepared by etching core copper sulphide in etching solution for 3 hours with a vigorous magnetic stirring. The etching solution consists of hydrochloric acid and toluene (v/v=1:1)

Table S2. Content of Cu in 0.5 M H_2SO_4 electrolyte before and after cycling test, determined by ICP-OES analysis.

Before cycling test	0.000 mg/L
After cycling test	0.003 mg/L

1. Supporting Figures S1-S6

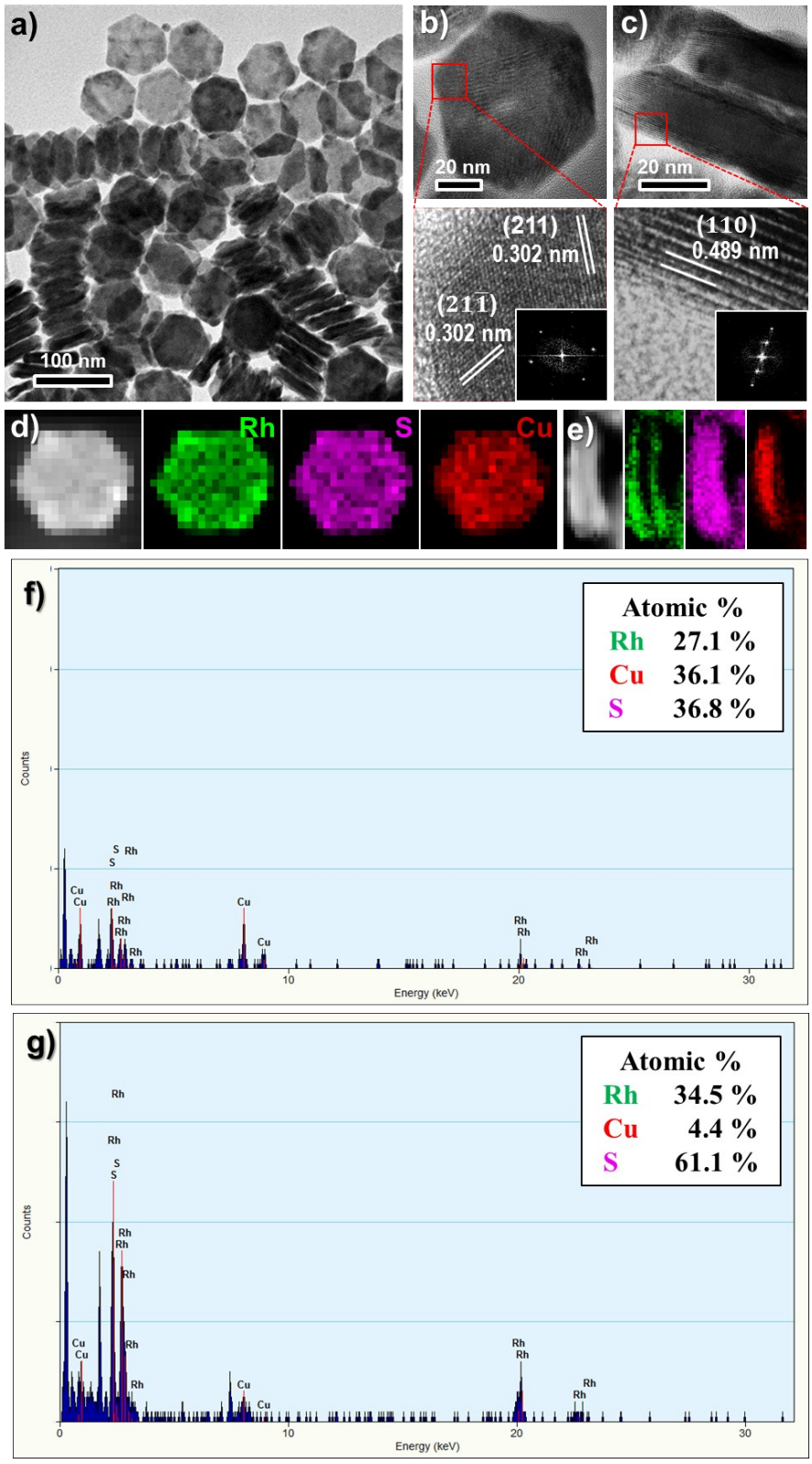

Fig. S1 a-c) TEM and HRTEM images with FFT analyses and d-e) elemental mapping spectra of $Cu_{1.94}S@Rh_2S_3$ nanocrystal. The elemental analysis for f) $Cu_{1.94}S@Rh_2S_3$ nanocrystals and g) hollow Rh_2S_3 nanocrystals

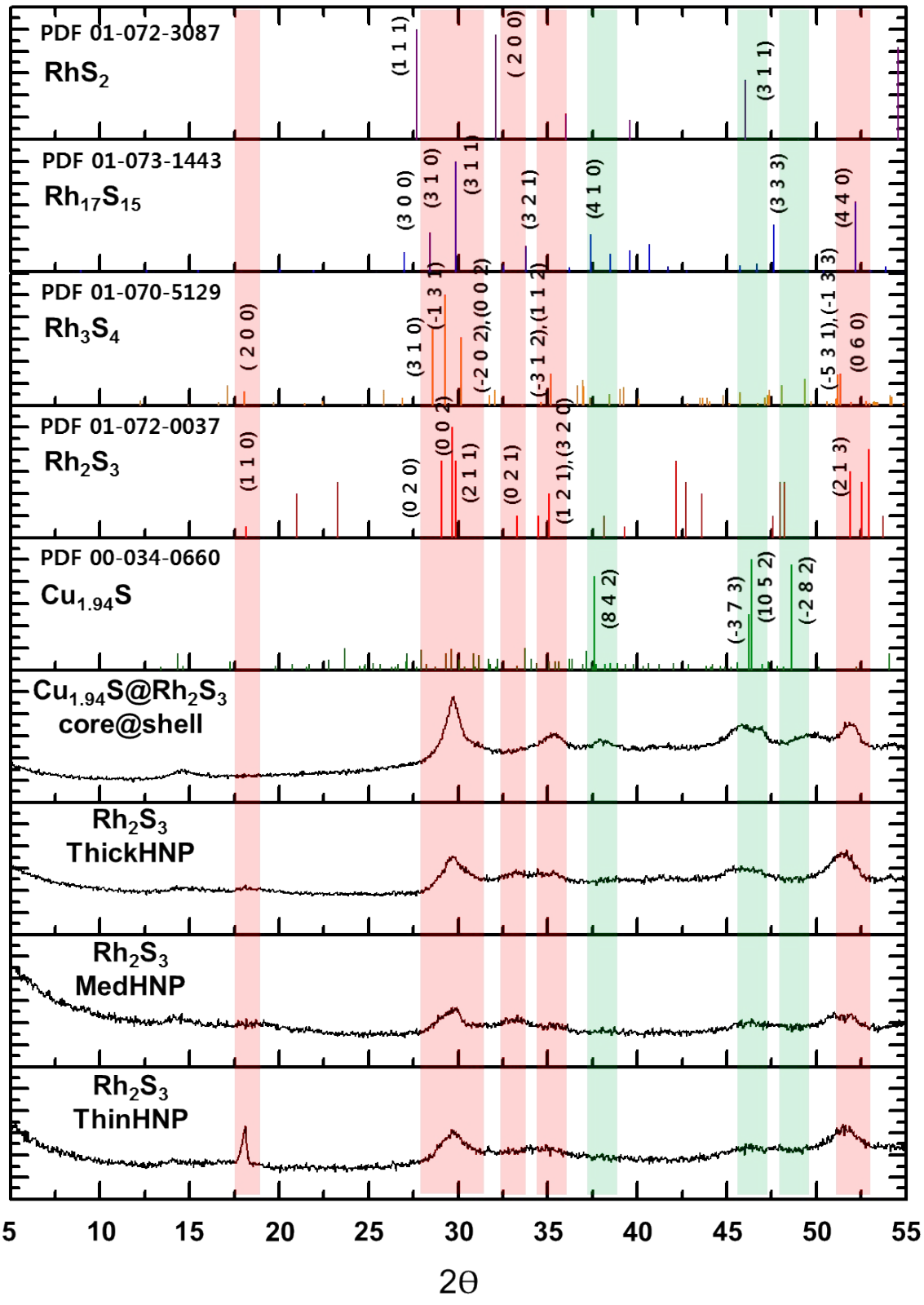

Fig. S2 XRD patterns of nanocrystals. The peaks from copper sulphide phase disappear after core etching.

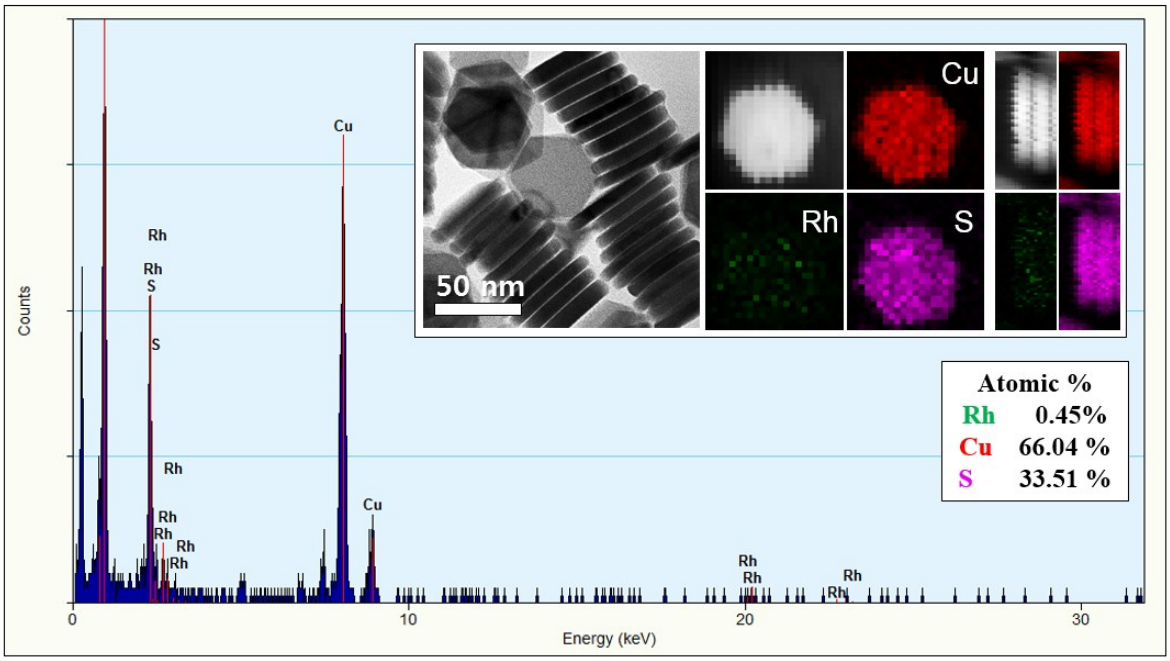

Fig. S3 TEM image and elemental analysis of reaction intermediates obtained at 2 min of reaction. Initially formed core of copper sulphide is clearly seen in elemental mapping with a low level Rh component.

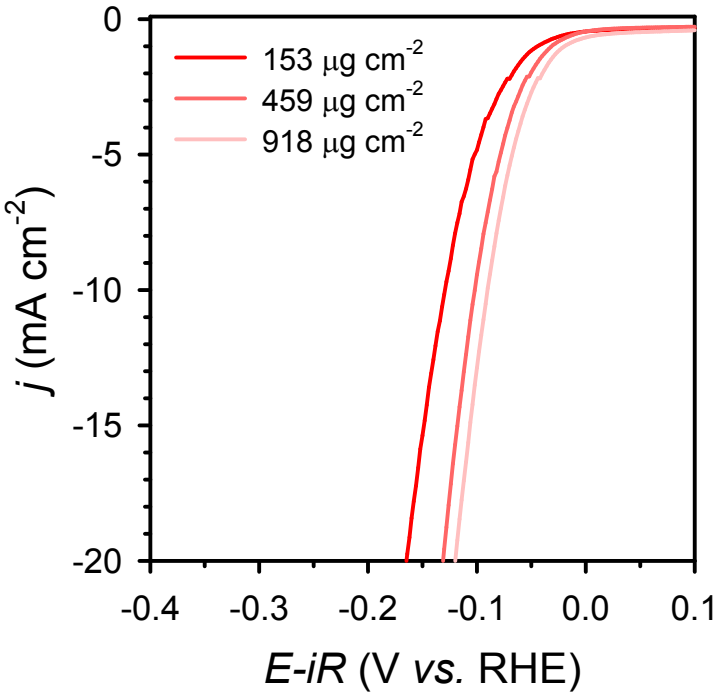

Fig. S4 Polarization curves for Rh_2S_3_ThickHNP/C samples with catalyst loadings of 153 μg cm^{-2}, 459 μg cm^{-2} and 918 μg cm^{-2} in 0.5 M H_2SO_4 with a scan rate of 2 mV s^{-1}.

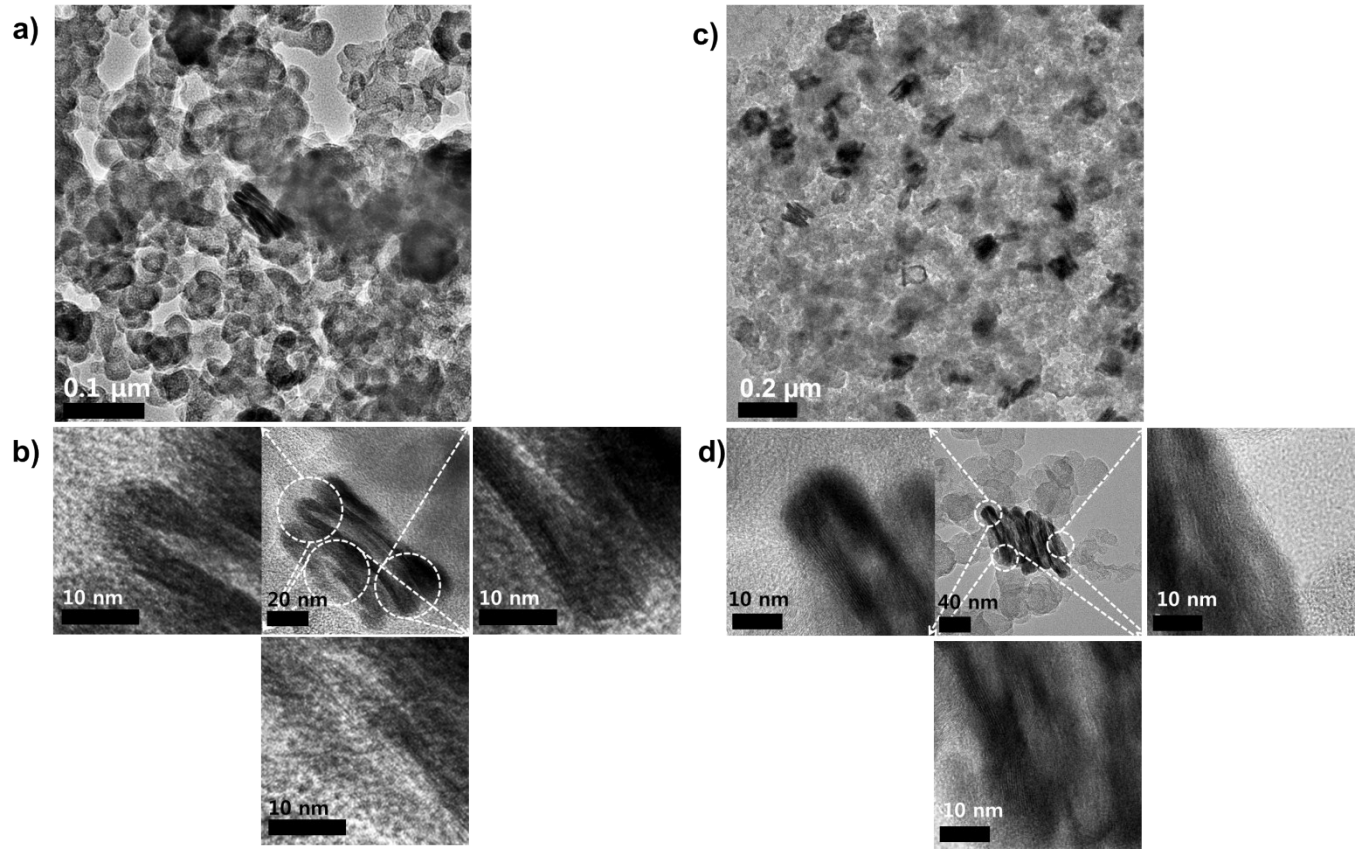

Fig. S5 TEM and HRTEM images of Rh_2S_3 nanocrystals a, b) before and c, d) after potential cycles. The structure of nanocrystals is well preserved and the distribution on carbon support is uniform without agglomeration.

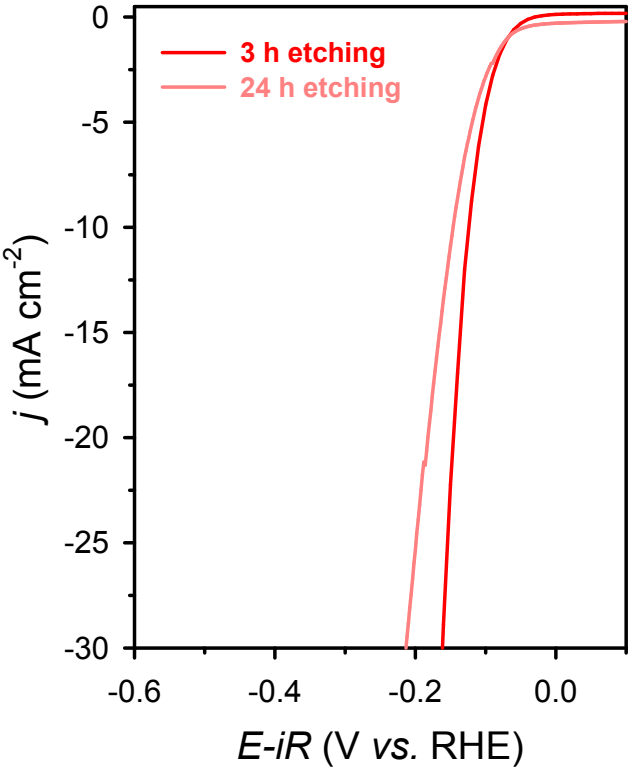

Fig. S6 a) Polarization curves for Rh_2S_3_ThickHNP/C_3 h etching and Rh_2S_3_ThickHNP/C_24 h etching in 0.5 M H_2SO_4 with a scan rate of 2 mV s^{-1}.