Electronic Supporting Information

Bimetallic Au@Rh core-shell nanostars with plasmon-enhanced catalytic performance in hydrogen evolution reaction

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Figure S1 Au nanoparticles were used for the synthesis of Au nanostars.



Figure S2 The as-prepared Au nanostars (a) and their size distribution (b).



Figure S3 TEM image of Rh MPs.



Figure S4 XPS survey spectrum of Au@Rh nanostars.



Figure S5 TEM images show the morphology evolution of Au@Rh nanostars with reaction time. The reaction time was (a) 0, (b) 1, (c) 2, (d) 4, (e) 6 and (f) 8 h. Scale bar for (a-f) is 50 nm. The inset of (b) shows a TEM image of a single Au@Rh nanostar particle consisting of Rh clusters on the Au nanostar, scale bar: 20 nm.



Figure S6 TEM images showing the morphology evolution of Au@Rh nanostars. The added volume Rh precursor was (a) 25, (b) 35, (c) 50, (d) 75, (e) 100 and (f) 125 uL. Scale bar for (a-f) is 50 nm. The inset of (f) shows a TEM image of a single Au@Rh nanostar particle consisting of Rh clusters on the Au nanostar, scale bar: 20 nm.



Figure S7 UV-vis spectra of Au@Rh nanostars with the increased amount of Rh precursor.



Figure S8 E-M field distribution of Au nanostar when the outside Rh clusters replaced by the Rh shells.



Figure S9 (a) The polarization curves of samples with adding different volume Rh precursor in 0.5 M H_2SO_4 solution and (b) the overpotentials of various catalysts at 10 mA cm⁻².



Figure S10 There were no significant changes in the temperature of the working electrode during the HER with (a) or without (b) the 808 nm laser illumination.



Figure S11 C_{dl} of Au@Rh nanostars under laser illumination and dark condition.



Figure S12 on–off j-t transients for Au nanostars, Rh MPs and Au@Rh nanostars with and without laser irradiation, respectively.



Figure S13 TEM images of Au@Rh nanostars before (a) and after (b) 5000 cycles of photoelectrocatalysis.



Figure S14 LSV polarization curves of Rh MPs (a) and Pt/C (b) before and after 5000 cycles of photo-electrocatalysis.

Element	Mass ratio %	Atom ratio %
Rh	48.2	64.04
Au	51.8	35.96

 Table S1 SEM-EDS data of Au@Rh nanostars.

Catalysts	Electrolyte	Overpotential at 10 mA cm ⁻² (mV)	Tafel solpe (mV dec ⁻¹)	Ref.
Au@Rh nanostars Under 808 nm light	0.5 M H ₂ SO ₄	28.5	29.3	This work
Rh/F-graphene	0.5 M H ₂ SO ₄	46	30	1
Rh-MoS2	0.5 M H ₂ SO ₄	47	24	2
Rh@CTF-1	0.5 M H ₂ SO ₄	58	37	3
RhCoB aerogels	0.5 M H ₂ SO ₄	12	30.7	4
Rh-Au-Si nanocomposite	0.5 M H ₂ SO ₄	60	24	5
PtRh DNAs	0.5 M H ₂ SO ₄	27	30	6
Rh-Ag-Si ternary composites	0.5 M H ₂ SO ₄	120	51	7
boron-doped RhFe alloy	0.5 M H ₂ SO ₄	25	32	8

Table S2 Comparison of HER activities in 0.5 M H_2SO_4 for Au@Rh nanostars with other reportedRh-based electrocatalysts.

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