Supporting Information

Gold Nanorod-Templated Synthesis of Polymetallic Hollow Nanostructures with Enhanced Electrocatalytic

Performances

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Fig. S1 TEM image of the original gold nanorods.



Fig. S2 (a) TEM image and (b) A HAADF-STEM image of hollow dumbbell-like nanorods of Au@PtAg.



Fig. S3 Line-scanning EDS of a single hollow dumbbell-like nanorods of Au@PtAg along the axial direction.



Fig. S4 Temporal evolution of Au, Pt and Ag during the formation of the HDB NRs.



Fig. S5 TEM image of the product obtained by the protocol for the HDB NRs with the reaction time for 16h.



Fig. S6 TEM images of the products obtained by the protocol for the HDB NRs except different concentrations of K_2PtCl_4 . (a) 0.2 and (b) 0.05 mM.



Fig. S7 TEM image of the product obtained by treating the reaction intermediate, solid PtAgcoated gold nanorods, with AA at 80°C in air.



Fig. S8 TEM images and size distributions of the products obtained by a series of control experiments at 80 °C. (a-c) Au nanorods; (d-f) Au nanorods + AA (air), (g-i) Au nanorods (air), and (j-l) Au nanorods + AA (N₂).



Fig. S9 TEM images of the products obtained by the protocol for the HDB NRs except different amounts of AA. (a) 80, (b) 40, and (c) 10uL.



Fig. S10 TEM images of the products obtained by the protocol for the HDB NRs except different concentrations of CTAB. (a) 0, (b) 50, (c) 100, and (d) 400 mM.



Fig. S11 Elemental maps of a single PtAu nanotube.



Fig. S12 TEM images of gold nanorods reacted with H_2PdCl_4 in the presence (a) or in the absence (b) of AgNO₃ at 80 °C.



Fig. S13 Chronoamperometric tests for the three nanostructures in 0.5 M HCOOH + 0.5 M H₂SO₄ solution at 0.3V.

	Au	Ag	Pt	Rh	Pd
Lattice constant (Å)	4.08	4.09	3.92	3.80	3.89
Lattice mismatch (%)		0.25	3.92	6.86	4.66
Surface energy (J m ⁻²)	1.50	1.24	2.49	2.70	2.0
Cohesive energy (eV atom ⁻¹)	3.81	2.95	5.84	5.75	3.89

Table S1 Structure parameters, surface energy and cohesive energy of Au, Ag, Pt, Rh and Pd 1

1 (a) C. Kittel, *Introduction to Solid State Physics*, 7th ed.; Wiley: New York, **1996**; (b) W. R. Tyson, W. A. Miller, *Surf. Sci.* 1977, **62**, 267-276.

Table S2 Electrochemical properties of different catalysts for formic acid electrooxidation

Catalyst Name	ECSA	Current Density (mA mg ⁻¹)			Current Density (mA cm ⁻²)		
	(m ² g ⁻¹)	Peak I	Peak II	PeakI/ PeakII	Peak I	Peak II	PeakI/ PeakII
Commercial Pt/C	38.9	5.85	83.5	0.07	0.0242	0.184	0.13
core-shell Au@PtAg NRs	62.5	171.8	407.3	0.42	0.280	0.657	0.43
HDB NRs of Au@PtAg	88.6	849.7	368.0	2.31	0.971	0.431	2.25
Nanotubes of PtAu	195.4	152.2	426.6	0.36	0.0799	0.222	0.36