

Electronic Supporting Information

Material Characterizations

Transmission electron microscopy (TEM) and high-resolution TEM were performed on a TECNAI G2 20 S-Twin operated at 200kV and TECNAI G2 F30 operated at 300 kV. X-ray diffraction (XRD) patterns were collected with a Rigaku UltimaIII diffractometer system using a graphite-monochromatized Cu-K α radiation at 40kV and 40mA. The BET (Brunauer -Emmett -Teller) surface area measurement was made using a conventional BET single-point N₂ physisorption apparatus (Micromeritics ASAP 2020 Surface Area and Porosity Analyzer).

Experimental Section

Preparation of Rh rods on Au@Pt nanowires (Fig. 1): Au@Pt Nanowires (1 mg) were dispersed in a mixture of Rh(acac)₃ (0.05 mmol, Strem, 99%), 1,2-hexadecanediol (0.93 mmol, Aldrich, 90%) and octadecylamine (15 mmol, Aldrich, technical grade, 90%) in a 100 mL Schlenk tube with a magnetic stirring at 100 °C. After being evacuated for 10 min with stirring at 100 °C, the solution was heated up to 130 °C at a heating rate of 5 °C/min and kept at the same temperature for 20 h under Ar gas condition. Finally, dark black precipitates could be obtained by cooling down the solution to room temperature and then by centrifugation with added methanol/toluene (v/v = 10 mL/15 mL).

Preparation of Rh plates on Au@Pt nanowires (Fig. 2): Au@Pt Nanowires (1 mg) were dispersed in a mixture of Rh(acac)₃ (0.05 mmol, Strem, 99%), 1,2-hexadecanediol (0.93 mmol, Aldrich, 90%) and octadecylamine (15 mmol, Aldrich, technical grade, 90%) in a 100 mL Schlenk tube with a magnetic stirring at 100 °C. After being evacuated for 10 min with stirring at 100 °C, the solution was heated up to 180 °C at a heating rate of 5 °C/min and kept at the same temperature for 14 h under Ar gas condition. Finally, dark black precipitates could be obtained by cooling down the solution to room temperature and then by centrifugation with added methanol/toluene (v/v = 10 mL/15 mL).

Preparation of entangled mane-like Rh branches on Au@Pt nanowires (Fig. 4): Au@Pt Nanowires (1 mg) were dispersed in a mixture of Rh(acac)₃ (0.05 mmol, Strem, 99%), 1,2-hexadecanediol (0.93 mmol, Aldrich, 90%) and octadecylamine (15 mmol, Aldrich, technical grade, 90%) in a 100 mL Schlenk tube with a magnetic stirring at 100 °C. After being evacuated for 10 min with stirring at 100 °C, the Schlenk tube containing the reaction mixture was directly placed in an oil bath, pre-heated to 180 °C, and kept at the same temperature for 14 h under Ar gas condition. Finally, dark black precipitates could be obtained by cooling down the solution to room temperature and then by centrifugation with added methanol/toluene (v/v = 10 mL/15 mL).

Preparation of single crystal Pt nanorods (Fig. S4): A slurry of Pt(acac)₂ (0.015 mmol, Aldrich, 99 %), hexadecyltrimethylammonium chloride (0.8 mmol, Aldrich, 98%), and octadecylamine (15 mmol, Aldrich, technical grade, 90%) was prepared in a 100 mL Schlenk tube with a magnetic stirring at 100 °C. After being evacuated for 10 min with stirring at 100 °C, the reaction mixture was purged with 1 atm CO gas. The Schlenk tube containing the reaction mixture was directly placed in an oil bath, pre-heated to 200 °C, and kept at the same temperature for 8 h under 1 atm CO. Finally, dark black precipitates could be obtained by cooling down the solution to room temperature and then by centrifugation with added methanol/toluene (v/v = 10 mL/15 mL).

Preparation of sample for BET analysis: The samples (each xxx mg) were prepared by heating at 150 °C for 1h with a flow of N₂ gas across the sample tube for removal of liberated contaminants.

Fig. S1. (a) Low and (b) high resolution TEM images of Au@Pt nanowires.

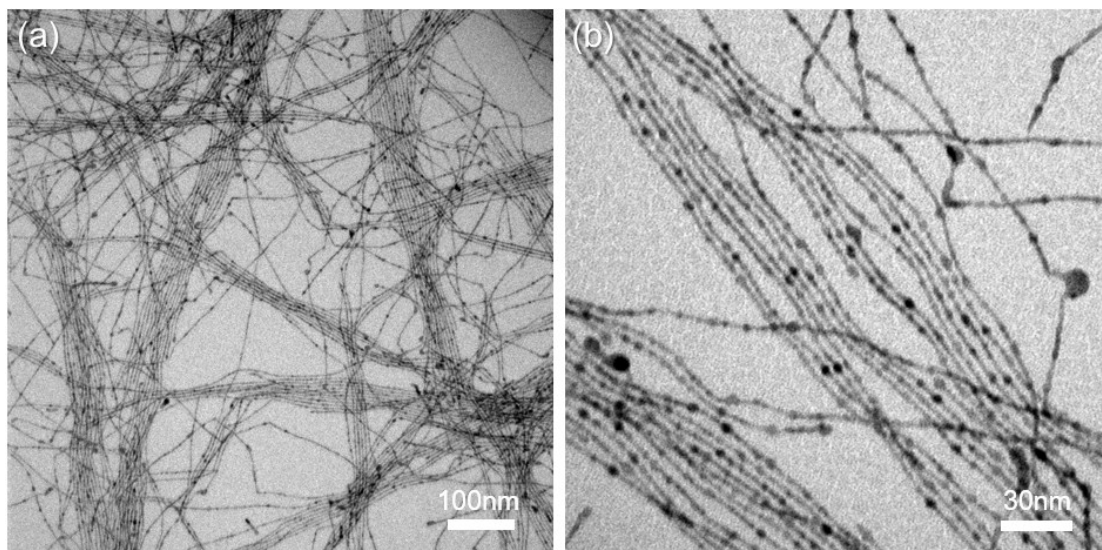


Fig. S2. TEM images of Rh nanorods on Au@Pt nanowire (ROW) recorded at various grid tilting angles: (a) 0°, (b) 15° and (c) 30°.

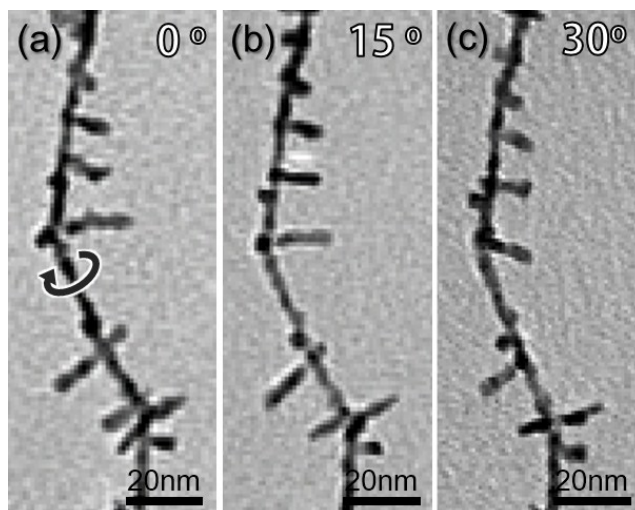


Fig. S3. TEM images of (a) Au@Pt nanoparticles and (b) Rh rods on Au@Pt nanoparticles. (c) HRTEM image of Rh nanorods grown on the twinning boundaries. Red arrows indicate the direction of Rh nanorod growth.

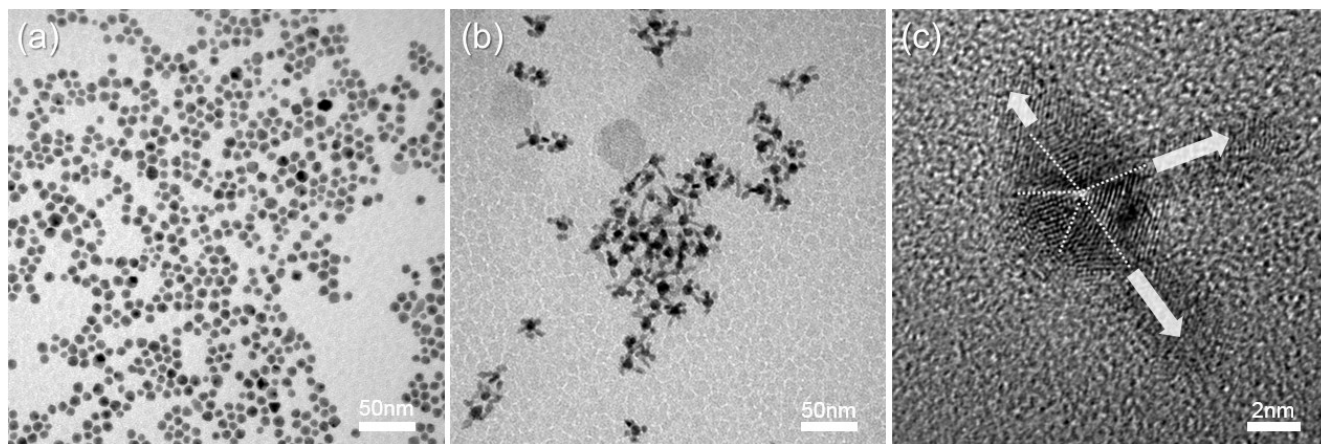


Fig. S4. (a) TEM image and (b) HRTEM image of single crystalline Pt nanorods (inset: corresponding FFT image). (c) TEM image for Ru/Pt nanostructures from Rh growth on single crystalline Pt nanorods.

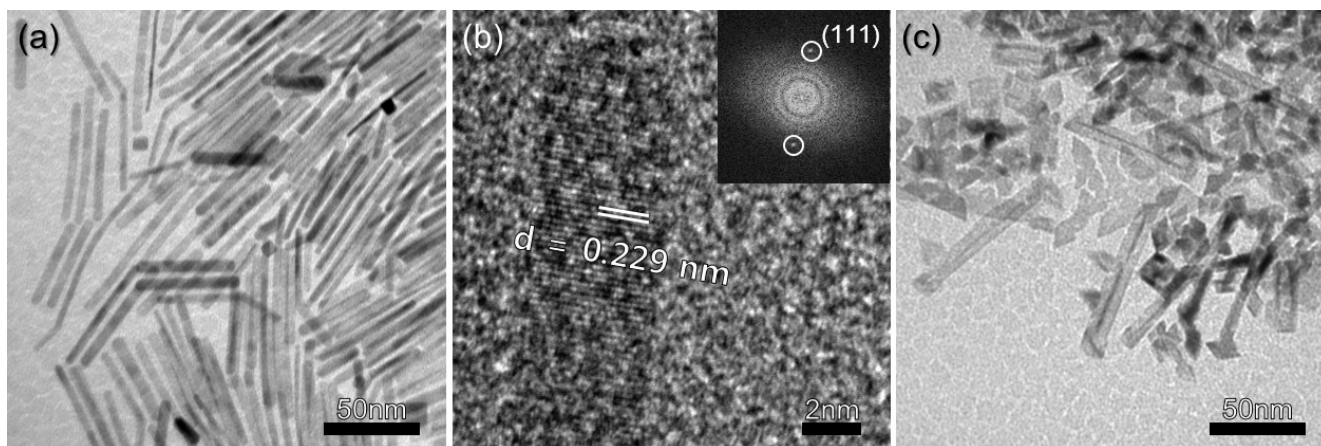


Fig. S5. (a) TEM image of triangular and trapezoidal-shaped Rh nanoplates with the corner angles of 60° or 120° . (b) Schematic diagram of Rh nanoplates. (c) Atomic array on a $\{111\}$ Rh facet. (d) Schematic diagram for Rh plate located perpendicular to the electron beam. (e) HRTEM image of the $\{111\}$ Rh plate: the lattice spacing is 0.135 nm . (f) Corresponding FFT pattern with the $[111]$ zone axis.

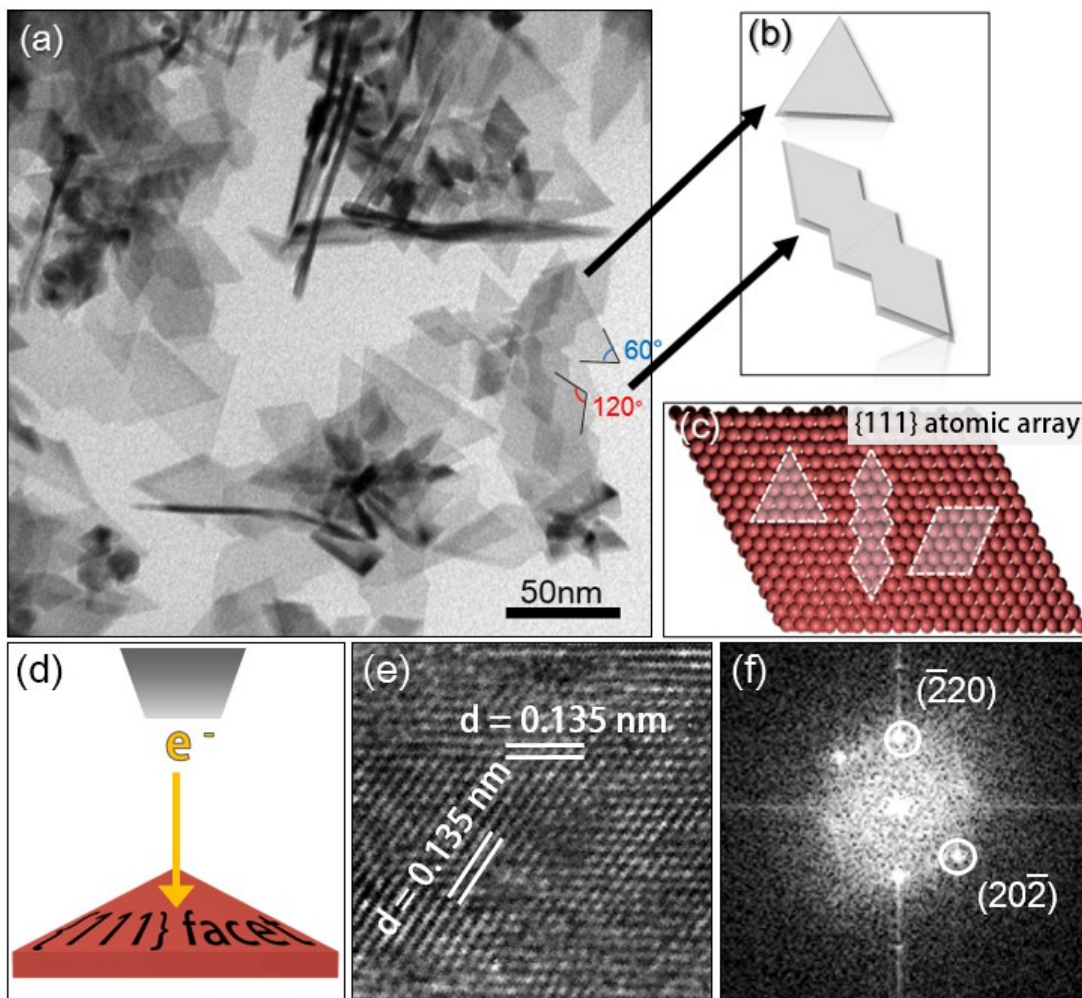


Fig. S6. (a) TEM image of Rh nanoplates on Au@Pt nanowires (POW) (inset: the histogram of inter-plate distance distribution for Rh nanoplates. The average inter-plate distance is about $1.05 (\pm 0.25)$ nm.) (b) Schematic image indicates the presence of squashed octadecylamine surfactant molecules between Rh nanoplates.

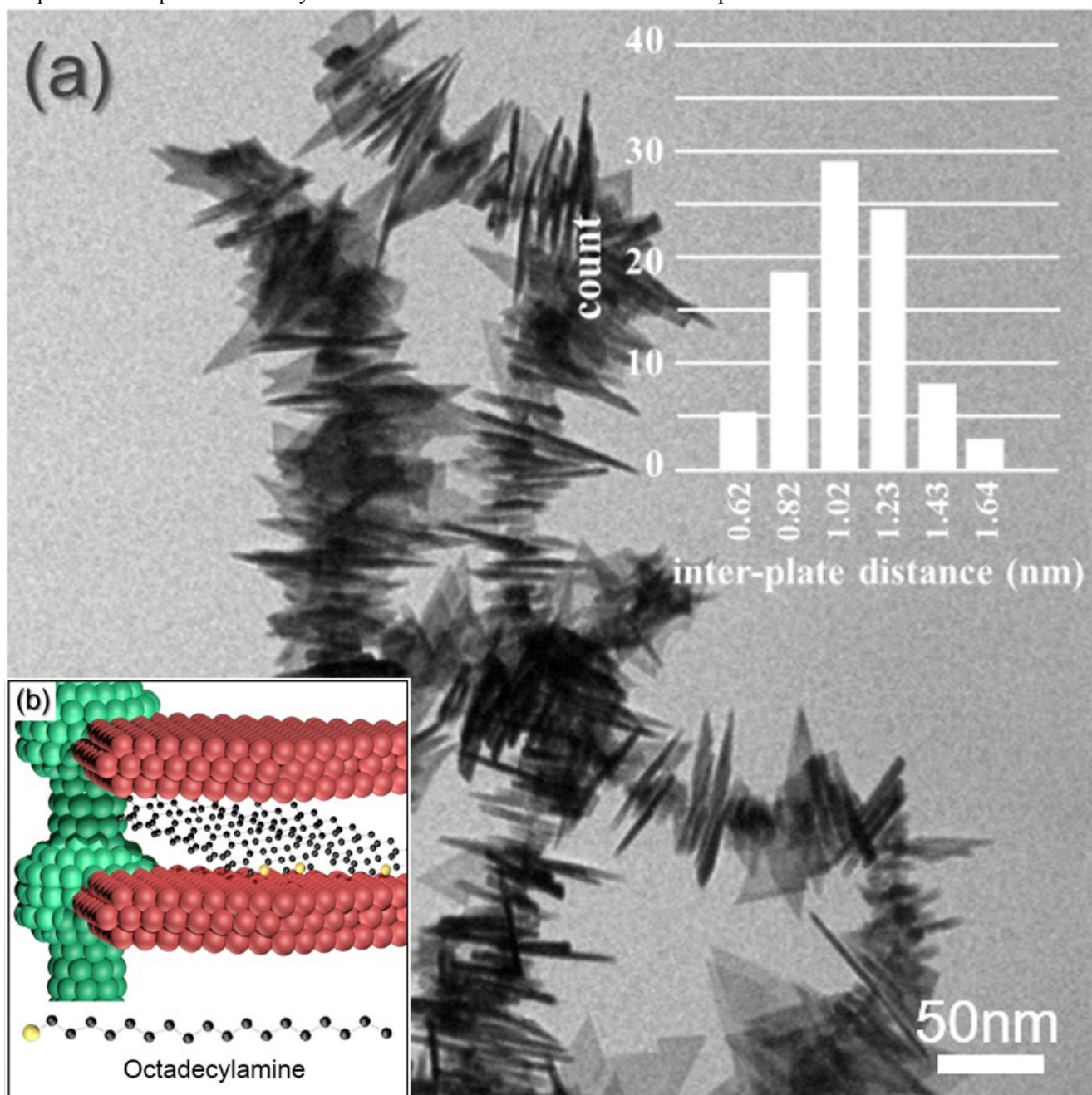


Fig. S7. TEM images of Rh nanoparticles synthesized under the same conditions for the synthesis of (a) Rh nanorods without Au@Pt nanowires and (b) Rh nanoplates without Au@Pt nanowires.

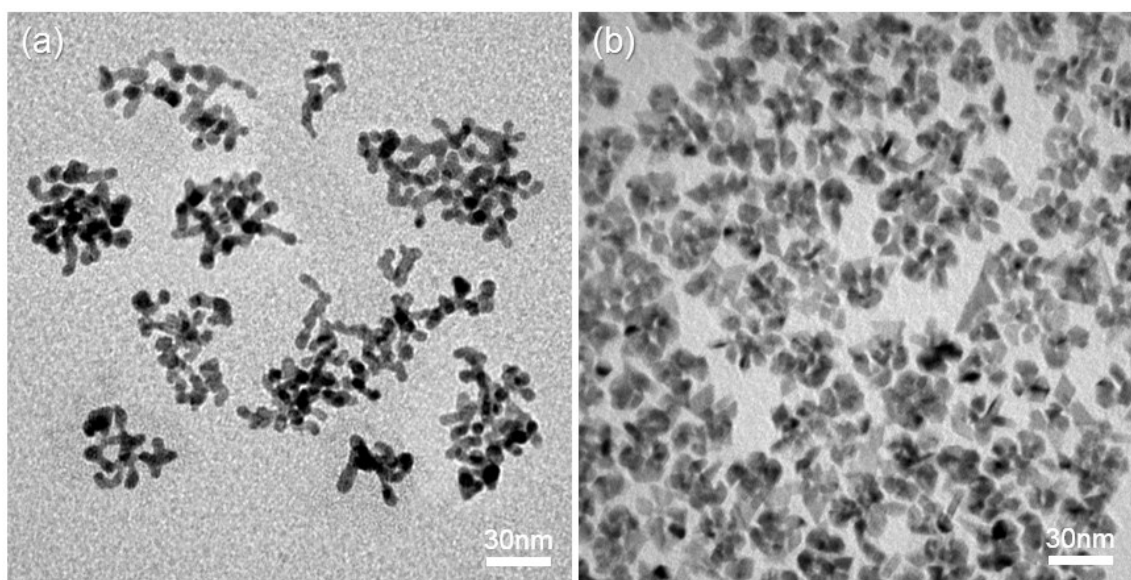


Fig. S8. TEM images of core-shell nanoparticles from growing Rh on spherical Au@Pt nanoparticles at 180 °C.

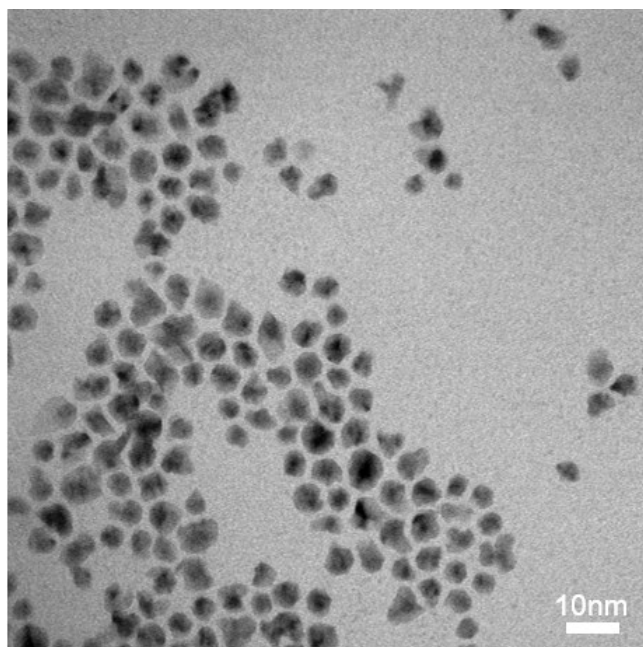


Fig. S9. Energy dispersive X-ray spectra and corresponding HAADF STEM images of (a) Rh nanorods on Au@Pt nanowire (ROW), (b) Rh nanoplates on Au@Pt nanowires (POW) and (c) entangled mane-like Rh on Au@Pt nanowire (EMOW).

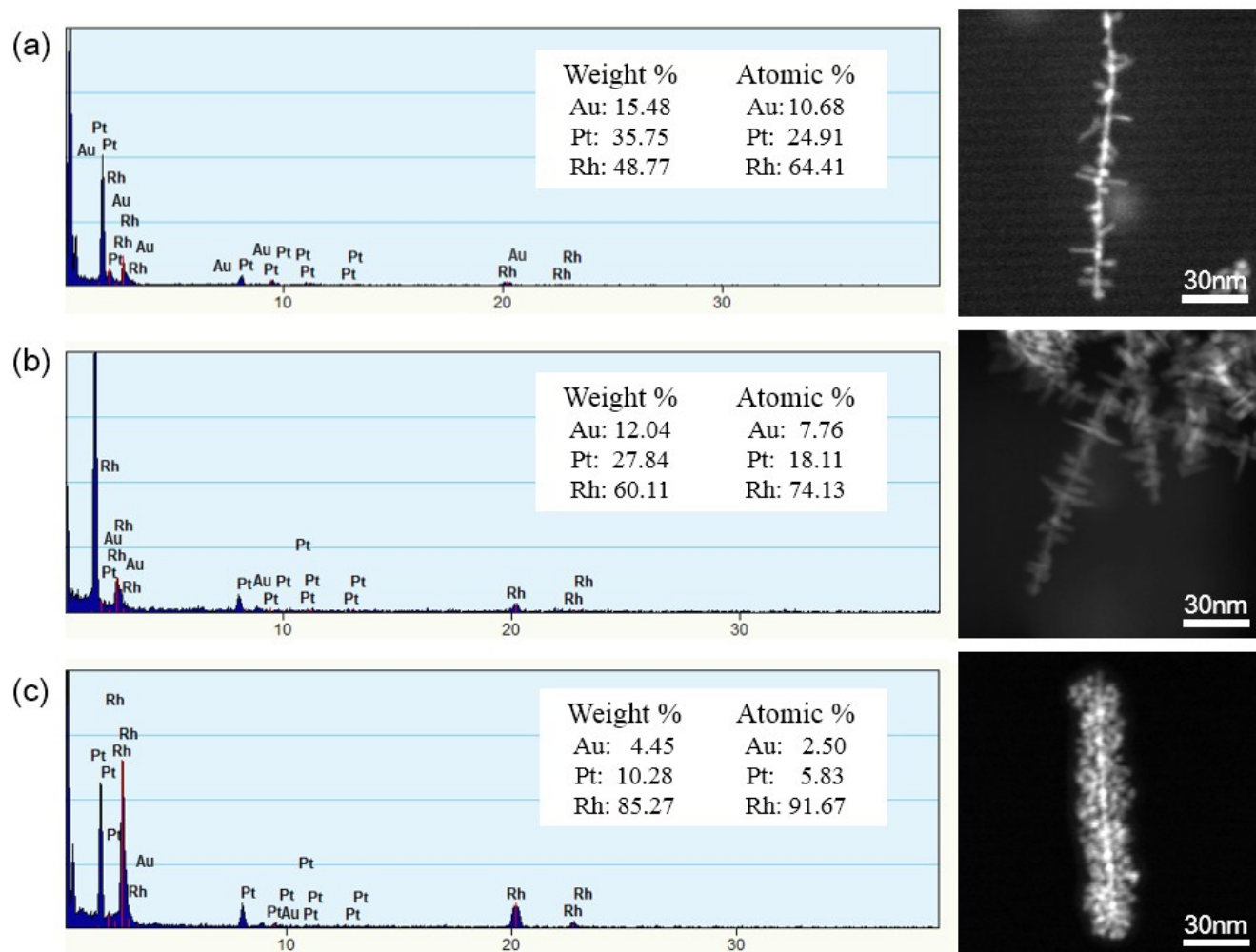
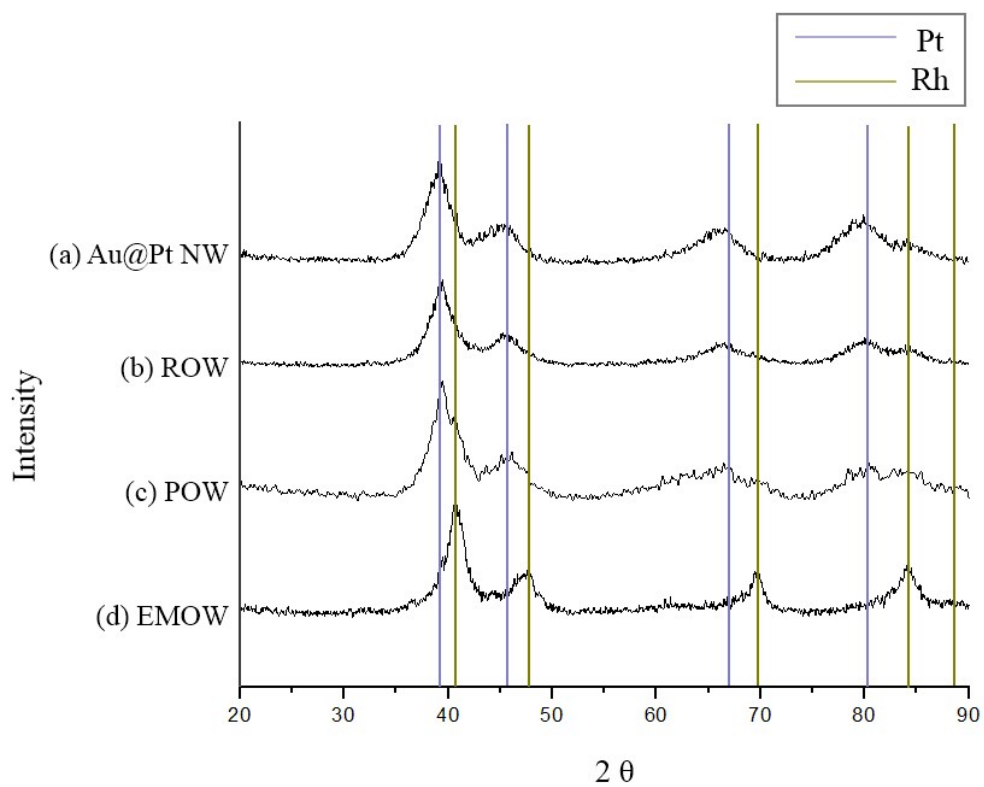


Fig. S10. XRD patterns of (a) Au@Pt nanowire, (b) Rh nanorods on Au@Pt nanowire (ROW), (c) Rh nanoplates on Au@Pt nanowire (POW) and (d) entangled mane-like Rh branches on Au@Pt nanowire (EMOW).



Calculation of surface area/weight of hierarchical Rh/Au@Pt nanostructures

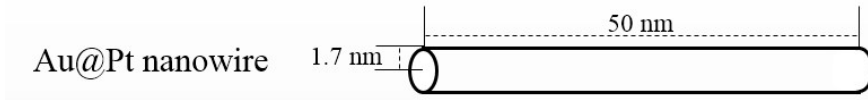


Fig. S11. Simplified model of Au@Pt nanowire.

(Average radius of the Au@Pt nanowires measured from 50 sites.)

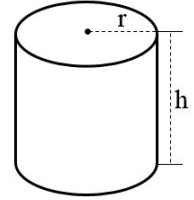
Surface area of cylinder, $A = 2\pi r^2 + 2\pi rh$

Volume of cylinder, $V = \pi r^2 h$

(where r is the radius of the circle, π is 3.14 and h is height of the cylinder)

$$A_{\text{Au@Pt nanowire}} = (2 \times 3.14 \times 1.7^2) + (2 \times 3.14 \times 1.7 \times 50) \approx 551.95 \text{ (nm}^2\text{)}$$

$$V_{\text{Au@Pt nanowire}} = 3.14 \times 1.7^2 \times 50 \approx 453.73 \text{ (nm}^3\text{)}$$



Apply for ROW structure:

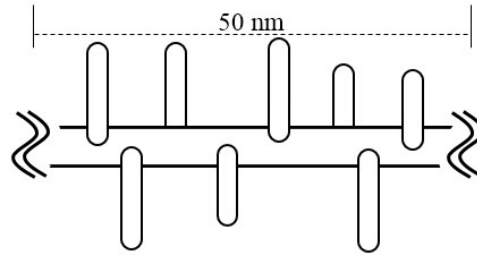


Fig. S12. Simplified model of Rh nanorods-on-wire structure.

(Average number Rh rods on the Au@Pt nanowires per 50 nm measured from 50 sites.)

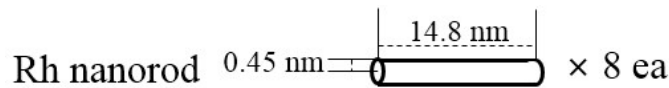


Fig. S13. Simplified model of Rh nanorod.

(Average radius and length of Rh rods measured from 50 Rh nanorods.)

$$A_{\text{ROW}} = n_{\text{Rh nanorod}} \times A_{\text{Rh nanorod}} + A_{\text{Au@Pt nanowire}}$$

$$V_{\text{ROW}} = n_{\text{Rh nanorod}} \times V_{\text{Rh nanorod}} + V_{\text{Au@Pt nanowire}}$$

(where $n_{\text{Rh nanorod}}$ is average number of Rh nanorods)

$$A_{\text{ROW}} = 8 \times \{(2 \times 3.14 \times 0.45^2) + (2 \times 3.14 \times 0.45 \times 14.8)\} + 551.95 \approx 896.73 \text{ (nm}^2\text{)}$$

$$V_{\text{ROW}} = 8 \times (3.14 \times 0.45^2 \times 14.8) + 453.73 \approx 529.01 \text{ (nm}^3\text{)}$$

$$m_{\text{ROW}} = \rho_{\text{ROW}} \times V_{\text{ROW}}$$

(where ρ_{ROW} is density of ROW)

$$\frac{100}{\rho_{ROW}} = \frac{x}{\rho_{Au}} + \frac{y}{\rho_{Pt}} + \frac{z}{\rho_{Rh}}$$

(x , y , z and $\rho_{Au}, \rho_{Pt}, \rho_{Rh}$ are % by weight and density of Au, Pt, and Rh, respectively.)

The energy dispersive X-ray spectroscopy (EDAX) analysis of ROW structures showed the weight % of Au, Pt and Rh: 15.48 %, 35.75 % and 48.77 % (Fig. S9). Density of Au, Pt and Rh: $19.3 \times 10^{-21} \text{ g/nm}^3$, $21.5 \times 10^{-21} \text{ g/nm}^3$ and $12.4 \times 10^{-21} \text{ g/nm}^3$.

$$\frac{100}{\rho_{ROW}} = \frac{15.48}{19.3 \times 10^{-21}} + \frac{35.75}{21.5 \times 10^{-21}} + \frac{48.77}{12.4 \times 10^{-21}}$$

$$\rho_{ROW} = 15.630 \times 10^{-21} \text{ g/nm}^3$$

$$m_{ROW} = 15.630 \times 10^{-21} \text{ g/nm}^3 \times 529.01 \text{ nm}^3 \approx 8268.5 \times 10^{-21} \text{ g}$$

$$\frac{\text{surface area}}{\text{weight}} = \frac{896.73 \text{ nm}^2}{8268.5 \times 10^{-21} \text{ g}} \approx 0.10845 \times 10^{21} \left(\frac{\text{nm}^2}{\text{g}} \right) \approx 108.45 \left(\frac{\text{m}^2}{\text{g}} \right)$$

Apply for POW structure:

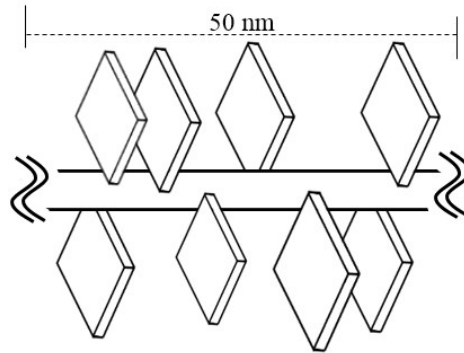
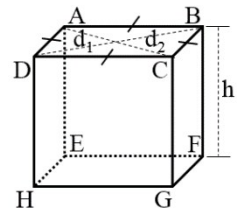


Fig. S14. Simplified model of Rh nanoplates-on-wire structure.

(Average number Rh plates on the Au@Pt nanowires per 50 nm measured from 50 sites.)

$$\text{Surface of rhombus pillar, } A = \left(2 \times \frac{d_1 \times d_2}{2} \right) + (2\sqrt{d_1^2 + d_2^2} \times h)$$

$$\text{Volume of rhombus pillar, } V = \frac{d_1 \times d_2}{2} \times h$$



(where d_1 is the length of one diagonal, d_2 is the length of second diagonal and h is height of the pillar)

Rh nanoplate

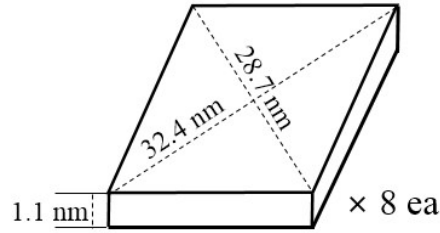


Fig. S15. Simplified model of Rh nanoplates.

(Average diagonals and height of Rh nanoplate measured from 50 Rh nanoplates.)

$$A_{\text{POW}} = 8 \times \left\{ \left(2 \times \frac{28.7 \times 32.4}{2} \right) + (2 \sqrt{28.7^2 + 32.4^2} \times 1.1) \right\} + 551.95 \approx 8672.8 \text{ (nm}^2\text{)}$$

$$V_{\text{POW}} = 8 \times \left(\frac{28.7 \times 32.4}{2} \times 1.1 \right) + 453.73 \approx 4545.2 \text{ (nm}^3\text{)}$$

The EDAX analysis of POW structures showed the weight % of Au, Pt and Rh: 12.04 %, 27.84 % and 60.11 % (Figure S9).

$$\frac{100}{\rho_{\text{POW}}} = \frac{12.04}{19.3 \times 10^{-21}} + \frac{27.84}{21.5 \times 10^{-21}} + \frac{60.11}{12.4 \times 10^{-21}}$$

$$\rho_{\text{POW}} = 14.779 \times 10^{-21} \text{ g/nm}^3$$

$$m_{\text{POW}} = 14.779 \times 10^{-21} \text{ g/nm}^3 \times 4545.2 \text{ nm}^3 \approx 67174 \times 10^{-21} \text{ g}$$

$$\frac{\text{surface area}}{\text{weight}} = \frac{8672.8 \text{ nm}^2}{67174 \times 10^{-21} \text{ g}} \approx 0.12911 \times 10^{21} \left(\frac{\text{nm}^2}{\text{g}} \right) \approx 129.11 \left(\frac{\text{m}^2}{\text{g}} \right)$$

Apply for EMOW structure:

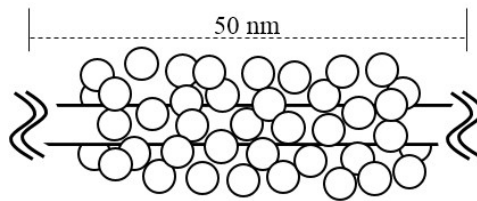
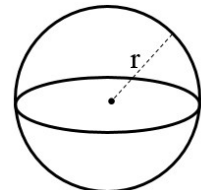


Fig. S16. Simplified model of entangled mane-like Rh branches-on-wire structure.

(Average number Rh branch units on the Au@Pt nanowires per 50 nm measured from 50 sites.)

$$\text{Surface of sphere, } A = 4\pi r^2$$

$$\text{Volume of sphere, } V = \frac{4}{3}\pi r^3$$



(where π is 3.14 and r is the radius of the sphere)

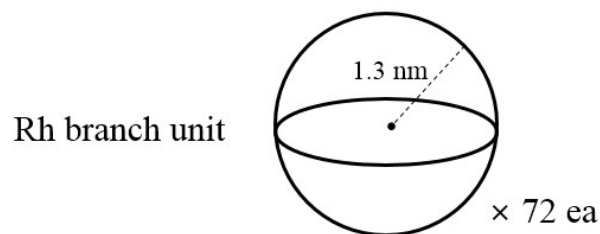


Fig. S17. Simplified model of Rh branch unit.

(Average radius of Rh branch units measured from 50 sites.)

$$A_{EMOW} = 72 \times \left(4 \times 3.14 \times 1.3^2 \right) + 551.95 \approx 2080.2 \text{ (nm}^2\text{)}$$

$$V_{EMOW} = 72 \times \left(\frac{4}{3} \times 3.14 \times 1.3^3 \right) + 453.75 \approx 1116.0 \text{ (nm}^3\text{)}$$

The EDAX analysis of EMOW structures showed the weight % of Au, Pt and Rh: 4.45 %, 10.28 % and 85.27 % (Figure S9).

$$\frac{100}{\rho_{EMOW}} = \frac{4.45}{19.3 \times 10^{-21}} + \frac{10.28}{21.5 \times 10^{-21}} + \frac{85.27}{12.4 \times 10^{-21}}$$

$$\rho_{EMOW} = 13.183 \times 10^{-21} \text{ g/nm}^3$$

$$m_{EMOW} = 13.183 \times 10^{-21} \text{ g/nm}^3 \times 1116.0 \text{ nm}^3 \approx 14712 \times 10^{-21} \text{ g}$$

$$\frac{\text{surface area}}{\text{weight}} = \frac{2080.2 \text{ nm}^2}{14712 \times 10^{-21} \text{ g}} \approx 0.14140 \times 10^{21} \left(\frac{\text{nm}^2}{\text{g}} \right) \approx 140.40 \left(\frac{\text{m}^2}{\text{g}} \right)$$