Electronic Supplementary Information

Epitaxial growth of unusual 4H hexagonal Ir, Rh, Os, Ru and Cu nanostructures on 4H Au nanoribbons

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Experimental section

Materials. Gold(III) chloride hydrate (HAuCl₄·xH₂O, ~50% Au basis), iridium(III) chloride hydrate (IrCl₃·xH₂O, reagent grade), rhodium(III) chloride hydrate (RhCl₃·xH₂O, crystalline, ≥ 99.9% trace metal basis), osmium(III) chloride hydrate (OsCl₃·xH₂O, reagent grade), ruthenium(III) chloride hydrate (RuCl₃·xH₂O, 99.98% trace metal basis), copper(II) nitrate trihydrate (Cu(NO₃)₂·3H₂O, purum p.a., 98.0–103% (RT)), potassium iodide (KI, ACS reagent, ≥ 99%), sodium iodide (NaI, ACS reagent, ≥ 99.5%), sodium bromide (NaBr, ACS reagent, ≥ 99%), oleylamine (technique grade, 70%), 1,2-dichloropropane (99%), chloroform (contains 100–200 ppm amylenes as stabilizer, ≥ 99.5%), hexane (technical grade) and the other chemicals used in the experiments without special mention were purchased from Sigma-Aldrich (Saint Louis, Missouri, USA). Ethanol (absolute, 99.9%) was bought from Merck (Nordic European Centre, Singapore). Milli-Q water (Milli-Q System, Millipore, Billerica, MA) was used in all the experiments. All the reagents were used as received without further purification.

Synthesis of 4H Au nanoribbons (NRBs). The 4H Au NRBS were synthesized according to our previously reported method with a slight modification.¹ Briefly, 330 µL of oleylamine, 5.31 mL of hexane, and 375 µL of 1,2-dichloropropane were successively added into a glass vial containing 6.12 mg of HAuCl₄·xH₂O. After the glass vial was tightly sealed, it was heated in a water bath at 58 °C for 16 h. The resulting product was collected by centrifugation (5,000 rpm, 1 min), washed four times with hexane, and then re-dispersed in 6.0 mL of hexane.

Synthesis of 4H/fcc bimetallic Au@Ir core-shell NRBS. The 4H/fcc Au@Ir NRBS were synthesized via the epitaxial growth of Ir on the 4H Au NRBS. First, the 4H Au NRBS (125 µL, in hexane) were carefully washed once with a mixture of hexane/ethanol (v/v = 1/2), twice with ethanol, and then re-dispersed in 250 µL of ethanol. Meanwhile, 100 µL of freshly prepared IrCl₃
solution (2 mM, in H$_2$O) and 50 µL of KI solution (400 mM, in H$_2$O) were mixed, denoted as Mixture A, and then heated at 95 °C for 20 min in an oil bath. After that, the aforementioned Mixture A and 120 µL of freshly prepared NaBH$_4$ solution (20 mM, in ethanol) were successively added into 250 µL of the as-prepared 4H Au NRB solution (in ethanol). The mixture in a sealed glass vial was then kept undisturbed at ambient conditions for 1 h. The resulting product was collected by centrifugation (7,000 rpm, 1 min), washed twice with ethanol, and then re-dispersed in ethanol (250 µL).

**Synthesis of 4H/fcc bimetallic Au@Rh core-shell NRBs.** The 4H/fcc Au@Rh NRBs were synthesized via the epitaxial growth of Rh on the 4H Au NRBs. First, the 4H Au NRBs (250 µL, in hexane) were carefully washed once with a mixture of hexane/ethanol (v/v = 1/2), twice with ethanol, and then re-dispersed in 250 µL of ethanol. Meanwhile, 100 µL of freshly prepared RhCl$_3$ solution (2 mM, in ethanol), 100 µL of NaBr solution (100 mM, in ethanol) and 10 µL of NaI solution (2 mM, in ethanol) were mixed, denoted as Mixture B, and then heated at 70 °C for 30 min in an oil bath. After that, the aforementioned Mixture B and 120 µL of freshly prepared NaBH$_4$ solution (20 mM, in ethanol) were successively added into 250 µL of the as-prepared 4H Au NRB solution (in ethanol). The mixture in a sealed glass vial was then kept undisturbed at ambient conditions for 1 h. The resulting product was collected by centrifugation (7,000 rpm, 1 min), washed twice with ethanol, and then re-dispersed in ethanol (250 µL).

**Synthesis of 4H/fcc bimetallic Au@Os core-shell NRBs.** The 4H/fcc Au@Os NRBs were synthesized via the epitaxial growth of Os on the 4H Au NRBs. First, the 4H Au NRBs (250 µL, in hexane) were carefully washed once with a mixture of hexane/ethanol (v/v = 1/2), twice with ethanol, and then re-dispersed in 250 µL of ethanol. After that, 100 µL of freshly prepared OsCl$_3$ solution (4 mM, in H$_2$O), 50 µL of H$_2$O and 120 µL of freshly prepared NaBH$_4$ solution (40 mM, in ethanol) were successively added into 250 µL of the as-prepared 4H Au NRB solution (in ethanol).
ethanol). The mixture in a sealed glass vial was then kept undisturbed at ambient conditions for 1 h. The resulting product was collected by centrifugation (7,000 rpm, 1 min), washed twice with ethanol, and then re-dispersed in ethanol (250 µL).

**Synthesis of 4H/fcc bimetallic Au@Ru core-shell NRBs.** The 4H/fcc Au@Ru NRBs were synthesized via the epitaxial growth of Ru on the 4H Au NRBs. First, the 4H Au NRBs (500 µL, in hexane) were carefully washed once with a mixture of hexane/ethanol (v/v = 1/2), twice with ethanol, and then re-dispersed in 250 µL of ethanol. After that, 100 µL of freshly prepared RuCl₃ solution (4 mM, in ethanol) and 120 µL of freshly prepared NaBH₄ solution (20 mM, in ethanol) were successively added into 250 µL of the as-prepared 4H Au NRB solution (in ethanol). The mixture in a sealed glass vial was then kept undisturbed at ambient conditions for 1 h. The resulting product was collected by centrifugation (7,000 rpm, 1 min), washed twice with ethanol, and then re-dispersed in ethanol (250 µL).

**Synthesis of 4H/fcc bimetallic Au@Cu core-shell NRBs.** The 4H/fcc Au@Cu NRBs were synthesized via the epitaxial growth of Cu on the 4H Au NRBs. First, the 4H Au NRBs (500 µL, in hexane) were carefully washed once with a mixture of hexane/ethanol (v/v = 1/1), and then re-dispersed in 250 µL of chloroform. After that, 250 µL of chloroform, 280 µL of ethanol, 100 µL of freshly prepared Cu(NO₃)₂ solution (8 mM, in ethanol) and 120 µL of freshly prepared NaBH₄ solution (40 mM, in ethanol) were successively added into 250 µL of the as-prepared 4H Au NRB solution (in chloroform). The mixture in a sealed glass vial was then kept undisturbed at ambient conditions for 1 h. The resulting product was collected by centrifugation (7,000 rpm, 1 min), washed once with a mixture of chloroform/ethanol (v/v = 1/1) and ethanol, respectively, and then re-dispersed in ethanol (250 µL).
Characterization. Transmission electron microscopy (TEM) samples of 4H/fcc Au@Ir, Au@Rh, Au@Os and Au@Ru NRBs were prepared by dropping 5.0 µL of the corresponding sample solutions onto full carbon-coated copper grids (200 mesh). TEM samples of 4H/fcc Au@Cu NRBs were prepared by dropping 5.0 µL of the corresponding sample solutions onto full carbon-coated nickel grids (200 mesh). After the TEM samples were dried at ambient conditions, TEM, high-resolution TEM (HRTEM) and high-angle annular dark-filed-scanning TEM (HAADF-STEM) images, selected-area electron diffraction (SAED) patterns, and STEM-energy dispersive X-ray spectroscopy (STEM-EDS) data were collected on a JEOL JEM-2100F transmission electron microscopy operated at 200 kV. The X-ray photoelectron spectroscopy (XPS) data were acquired with a Theta Probe electron spectrometer (ESCA-Lab-200i-XL, Thermo Scientific).
**Figure S1.** (a) Low- and (b) high-magnification TEM images of the synthesized 4H Au NRBs. (c) SAED pattern of a typical 4H Au NRB taken along the [110]_{4H} zone axis. (d) A representative HRTEM image of the 4H Au NRB.
Figure S2. XPS spectra of alternating 4H/fcc Au@Ir core-shell NRBs showing the core level peaks of (a) Au 4f and (b) Ir 4f.

Figure S3. A representative STEM-EDS spectrum of the synthesized 4H/fcc bimetallic Au@Ir NRBs, giving average Au/Ir atomic ratio of approximately 1.00/0.99.
Figure S4. (a) HAADF-STEM image and (b) corresponding STEM-EDS line scanning profile of a representative 4H/fcc bimetallic Au@Ir NRB.

Figure S5. A representative XRD pattern of the synthesized 4H/fcc bimetallic Au@Ir NRBS.
Figure S6. A representative STEM-EDS spectrum of the synthesized 4H/fcc bimetallic Au@Rh NRBs, giving average Au/Rh atomic ratio of approximately 1.00/0.75.

Figure S7. (a) HAADF-STEM image and (b) corresponding STEM-EDS line scanning profile of a representative 4H/fcc bimetallic Au@Rh NRB.
**Figure S8.** A representative STEM-EDS spectrum of the synthesized 4H/fcc bimetallic Au@Os NRBs, giving average Au/Os atomic ratio of approximately 1.00/0.81.

**Figure S9.** (a) HAADF-STEM image and (b) corresponding STEM-EDS line scanning profile of a representative 4H/fcc bimetallic Au@Os NRB.
Figure S10. A representative STEM-EDS spectrum of the synthesized 4H/fcc bimetallic Au@Ru NRBs, giving average Au/Ru atomic ratio of approximately 1.00/0.71.

Figure S11. (a) HAADF-STEM image and (b) corresponding STEM-EDS line scanning profile of a representative 4H/fcc bimetallic Au@Ru NRB.
**Figure S12.** XPS spectra of alternating 4H/{\textit{fcc}} Au@Rh, Au@Os, and Au@Ru core-shell NRBs showing the core level peaks of (a) Au 4f and (b) Rh 3d, (c) Au 4f and (d) Os 4f, and (e) Au 4f and (f) Ru 3d{\textsubscript{5/2}}, respectively.
Figure S13. Representative XRD patterns of the synthesized $4\text{H}/fcc$ bimetallic (a) Au@Rh, (b) Au@Os and (c) Au@Ru NRBs.
Figure S14. XPS spectra of alternating 4H/fcc Au@Cu core-shell NRBs showing the core level peaks of (a) Au 4f and (b) Cu 2p$_{3/2}$.

Figure S15. A representative STEM-EDS spectrum of the synthesized 4H/fcc bimetallic Au@Cu NRBs, giving average Au/Cu atomic ratio of approximately 1.00/0.45.
Figure S16. (a) HAADF-STEM image and (b) corresponding STEM-EDS line scanning profile of a representative 4H/fcc bimetallic Au@Cu NRB.

Figure S17. A representative XRD pattern of the synthesized 4H/fcc bimetallic Au@Cu NR Bs.
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