## **Supplementary Information**

## Selective control of fcc and hcp crystal structures in Au–Ru solid-solution alloy nanoparticles

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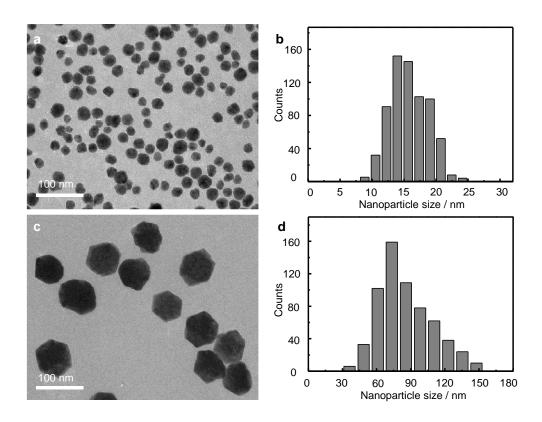
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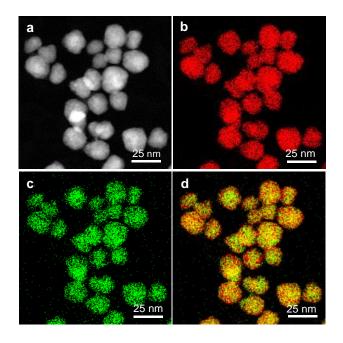
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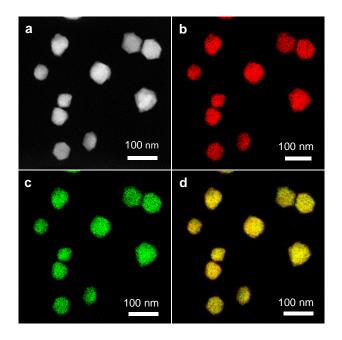
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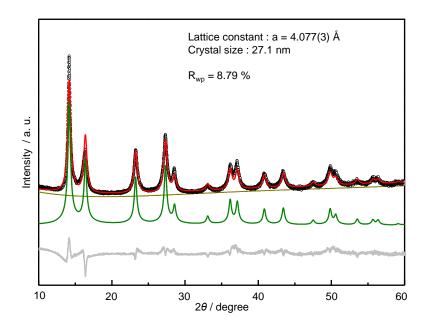
**Supplementary Figure 1.** (a) TEM image of the synthesized fcc-AuRu<sub>3</sub> NPs. (b) Size distributions of the nanoparticles in (a). (c) TEM image of the synthesized hcp-AuRu<sub>3</sub> NPs. (d) Size distributions of the nanoparticles in (c).



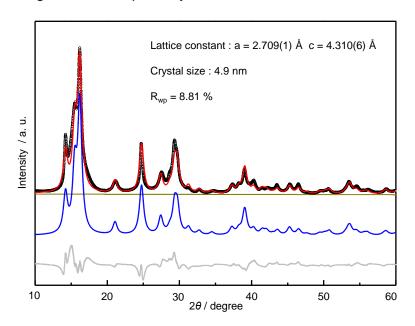
**Supplementary Figure 2.** (a) Low magnification HAADF-STEM image of fcc-AuRu<sub>3</sub> NPs. (b) Ru-L STEM-EDX map of (a). (c) Au-M STEM-EDX map of (a). (d) Overlay image of (b) and (c) (red, Ru; green, Au).



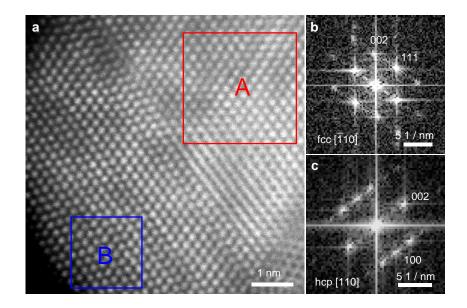
**Supplementary Figure 3.** (a) Low magnification HAADF-STEM image of hcp-AuRu<sub>3</sub> NPs. (b) Ru-L STEM-EDS map of (a). (c) Au-M STEM-EDX map of (a). (d) Overlay image of (b) and (c) (red, Ru; green, Au).



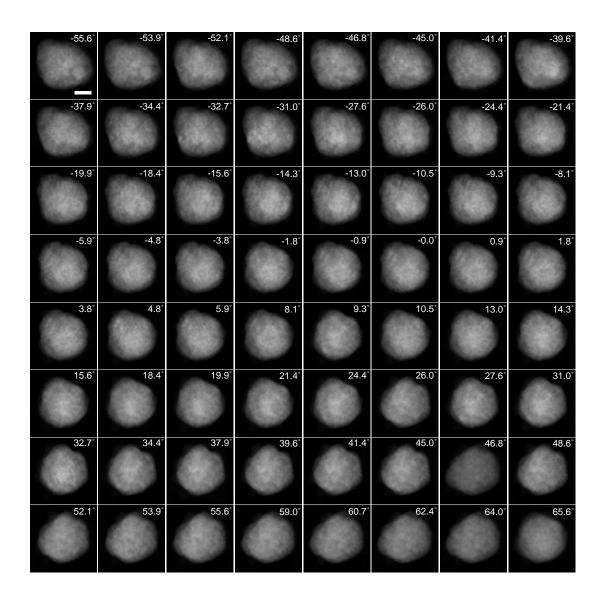
**Supplementary Figure 4.** Rietveld refinement for Au NPs. The diffraction patterns are shown as black circles. The calculated patterns are shown as red lines. The difference profile, the background profile, and the fitting curves of the fcc components are shown as grey, brown and green lines, respectively.



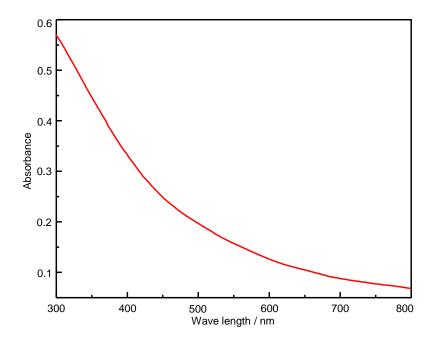
**Supplementary Figure 5.** Rietveld refinement for Ru NPs. The diffraction patterns are shown as black circles. The calculated patterns are shown as red lines. The difference profile, the background profile, and the fitting curves of the hcp components are shown as grey, brown and blue lines, respectively.



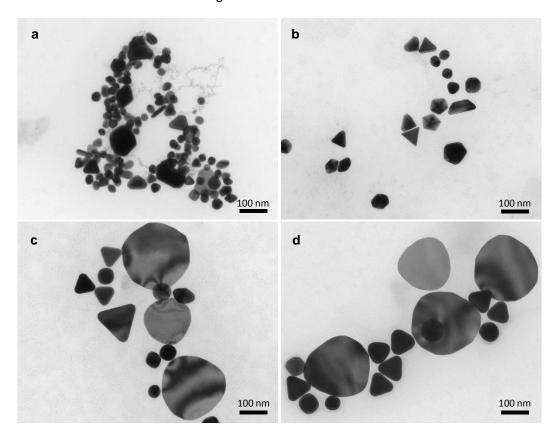
**Supplementary Figure 6.** (a) Low magnification HAADF-STEM image of the fcc-AuRu<sub>3</sub> NP. (b) The corresponding FFT pattern of the red square region A in (a). (c) The corresponding FFT pattern of the blue square region B in (a).



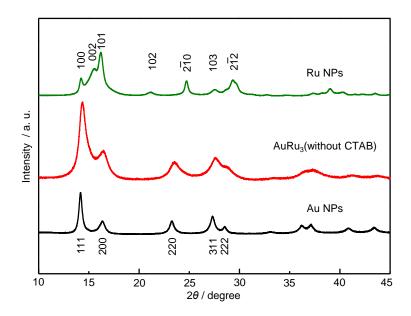
**Supplementary Figure 7.** Experimental tilt series obtained from a fcc-AuRu<sub>3</sub> NP. 64 projection images with a tilt range from -55.6° to +65.6° were measured using a JEM-ARM200F operated at 120 kV. The scale bar is 5 nm.



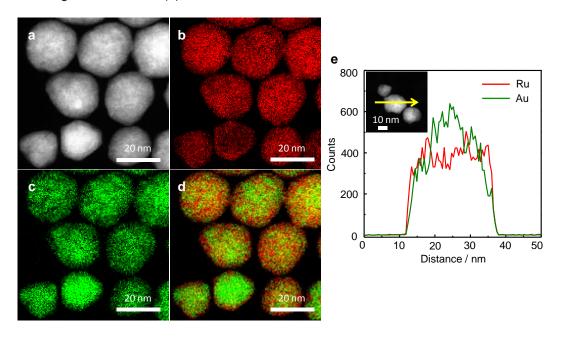
**Supplementary Figure 8.** UV-Vis spectrum of Ru NPs in the EG solution. The concentration of Ru NPs is 0.04 mg ml<sup>-1</sup>.



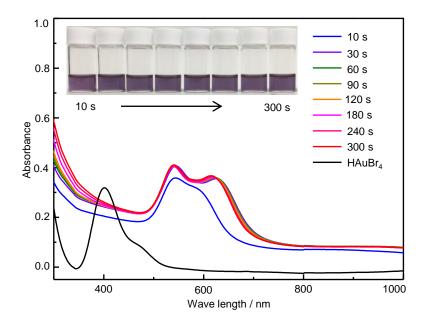
**Supplementary Figure 9.** TEM images of Au NPs at different reaction time during the reduction process of HAuBr<sub>4</sub> with CTAB in DEG. (a) 90 s, (b) 120 s, (c) 180 s, (d) 240 s.



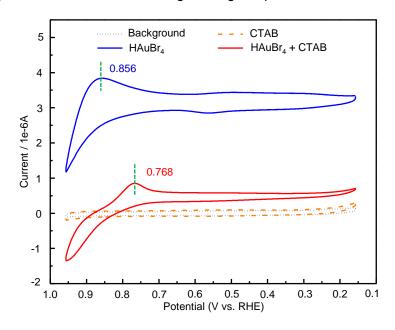
**Supplementary Figure 10.** Synchrotron XRD patterns of AuRu<sub>3</sub> NPs prepared using HAuBr<sub>4</sub> and RuCl<sub>3</sub> as metal precursors without using CTAB at 303 K. The radiation wavelength was 0.57865(1) Å.



**Supplementary Figure 11.** (a) HAADF-STEM image of AuRu<sub>3</sub> NPs (synthesized using HAuBr<sub>4</sub> and RuCl<sub>3</sub> as metal precursors without using CTAB), (b) Ru-L STEM-EDX map and (c) Au-M STEM-EDX map. (d) Overlay image of (b) and (c) (red, Ru; green, Au). (e) EDX line profiles of AuRu<sub>3</sub> NPs across the NP along the arrow shown in the inset figure.



**Supplementary Figure 12.** UV-Vis spectra of HAuBr<sub>4</sub> in DEG with increasing reaction time. Insert photo shows the colour change during this process.



**Supplementary Figure 13.** Cyclic voltammograms of  $HAuBr_4$  and  $HAuBr_4$  with CTAB. The cyclic voltammograms were measured in a 0.05 mmol  $L^{-1}$  sulfuric acid aqueous solution at 0.02 V s<sup>-1</sup>.