

Supplementary Information

Heterophase fcc-2H-fcc gold nanorods

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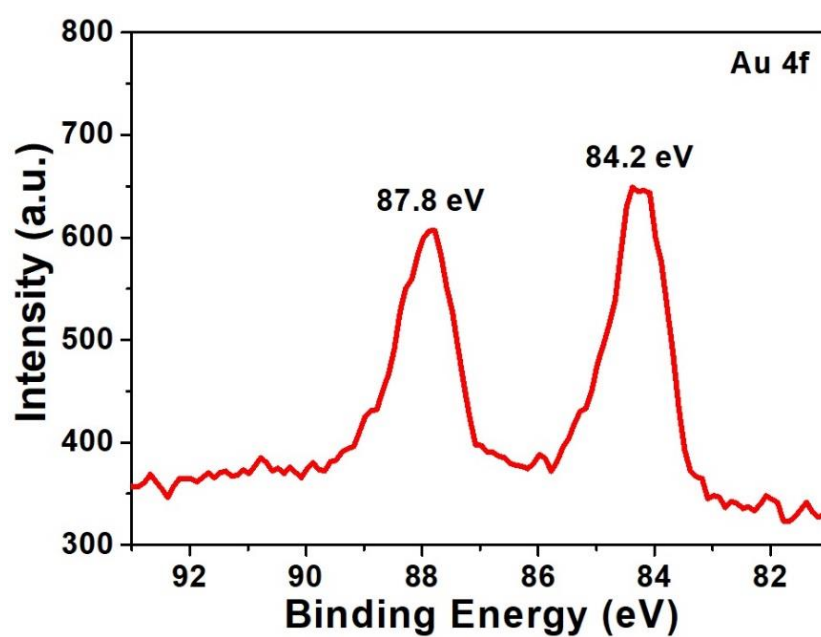
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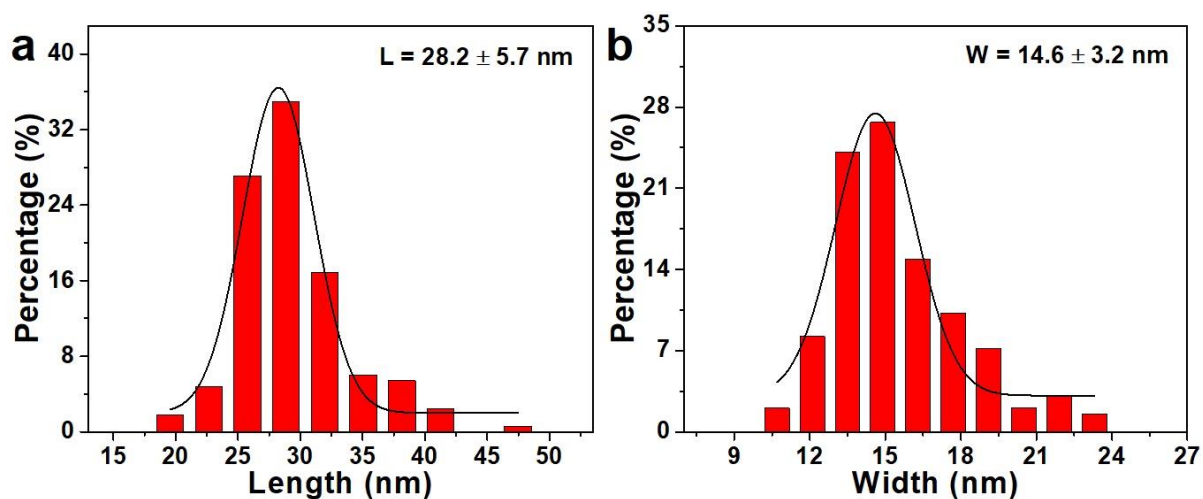
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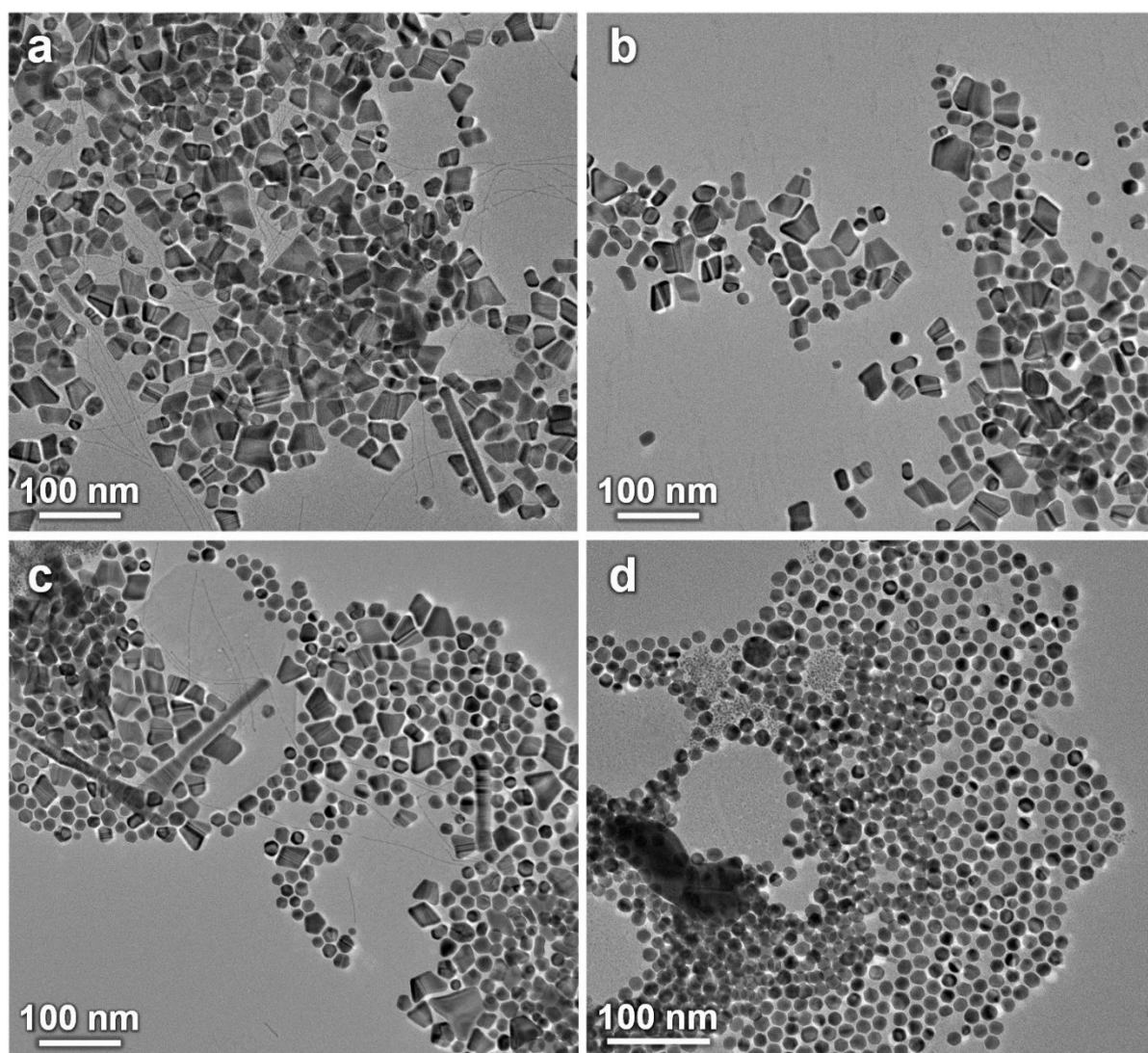
Supplementary Figures



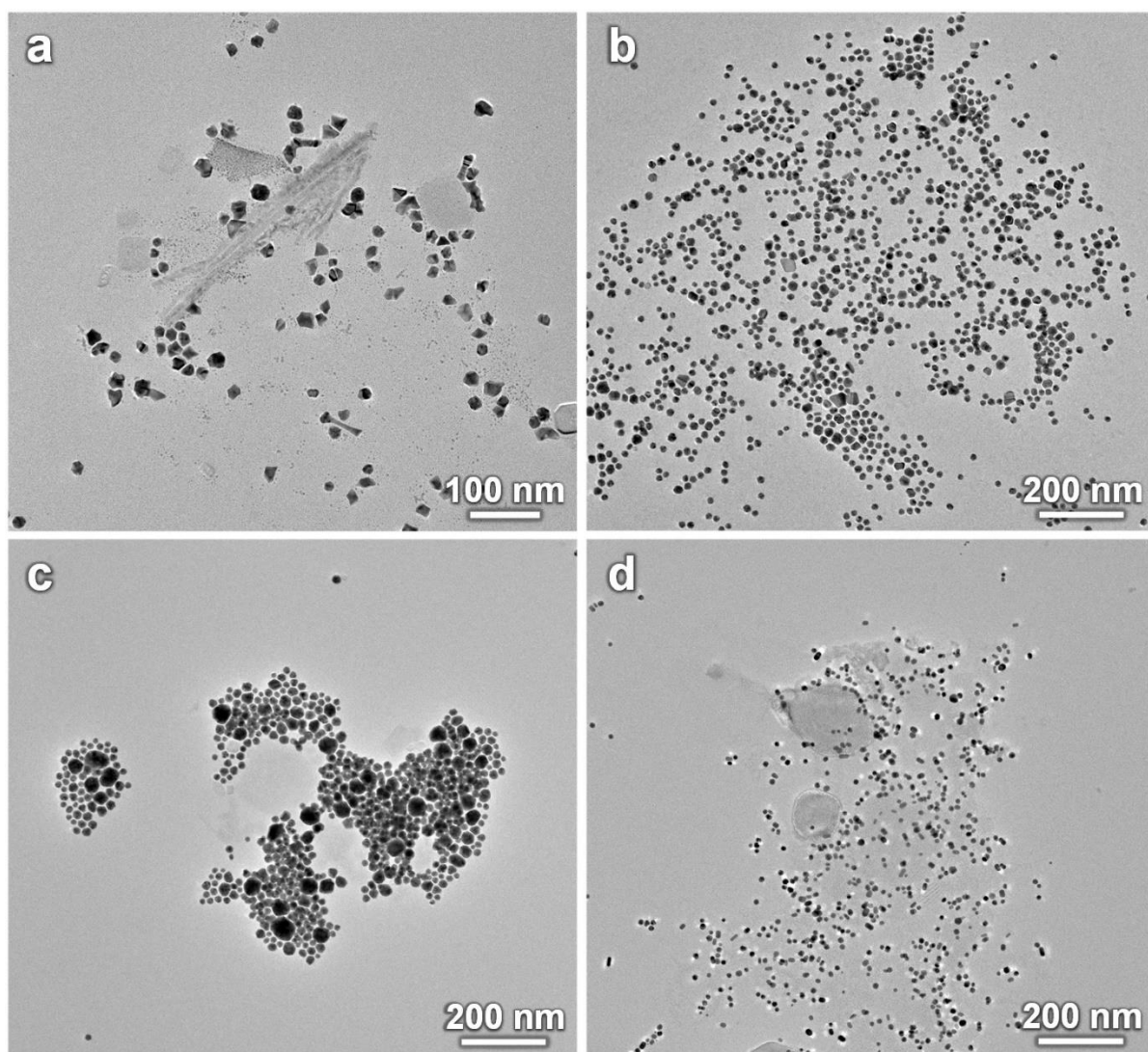
Supplementary Figure 1 | XPS analysis of Au chemical state. The XPS spectrum of fcc-2H-fcc Au NRs, showing the core level peaks of Au 4f doublet. The position of Au 4f doublet identifies the metallic state of Au in the obtained fcc-2H-fcc Au NRs.



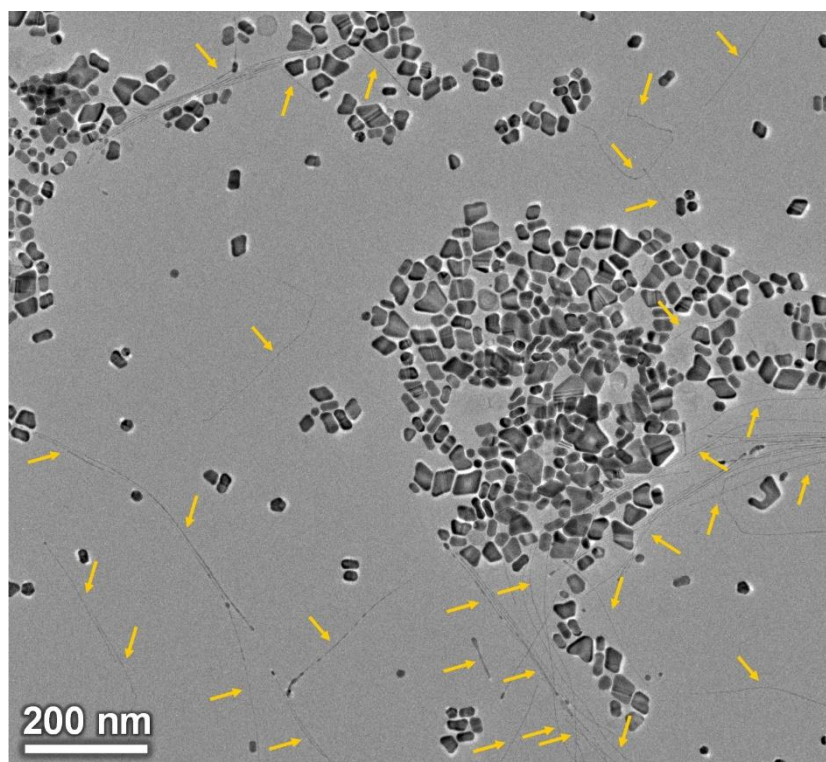
Supplementary Figure 2 | Size distribution analysis of fcc-2H-fcc Au NRs. **a**, Statistical analysis of the length of Au NRs measured by TEM, in which 28.2 nm is the average length and 5.7 nm is the standard deviation. **b**, Statistical analysis of the width of Au NRs measured by TEM, in which 14.6 nm is the average width and 3.2 nm is the standard deviation. The curves in **a** and **b** were obtained by fitting the data using a Gaussian function.



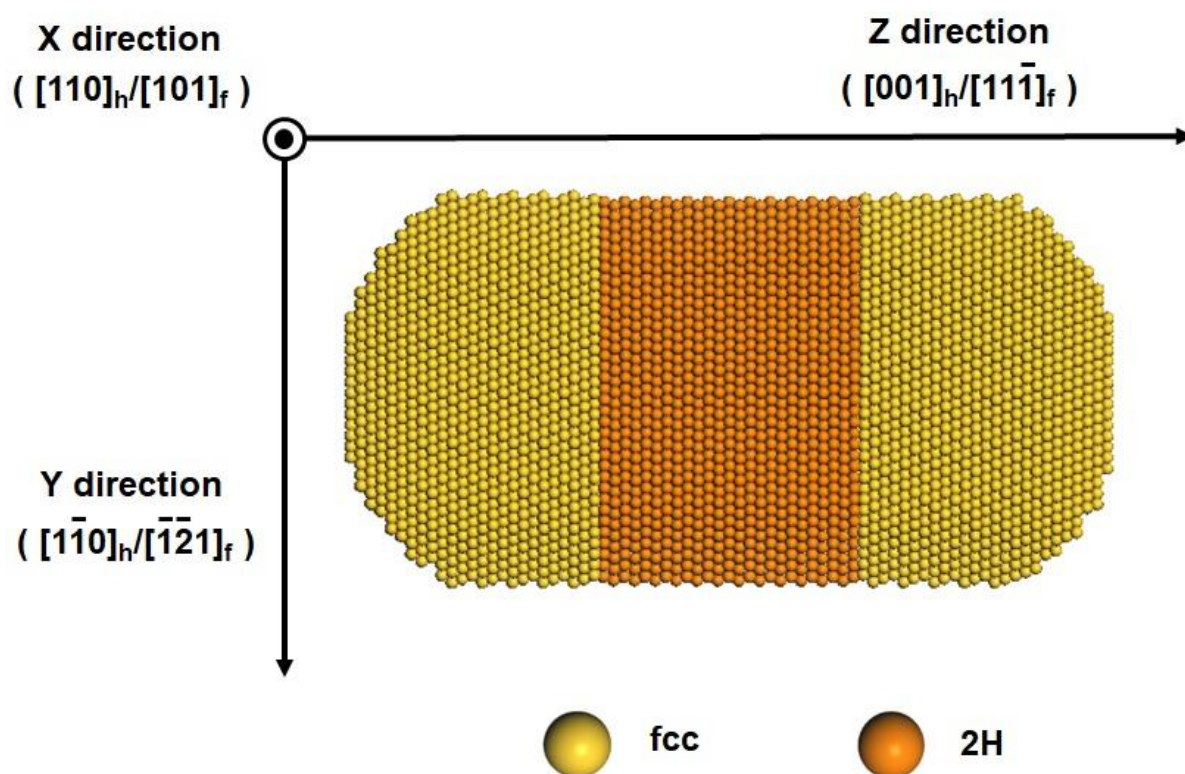
Supplementary Figure 3 | The effect of Au precursors. a-d, TEM images of Au nanostructures obtained by replacing the potassium gold(III) chloride (KAuCl_4) with other Au precursors, i.e., (a) tetrachloroauric(III) acid (HAuCl_4), (b) trichloro(pyridine)gold(III) ($\text{AuCl}_3 \cdot \text{Py}$), (c) gold(III) chloride (AuCl_3), and (d) gold(III) acetate ($\text{Au}(\text{ac})_3$).



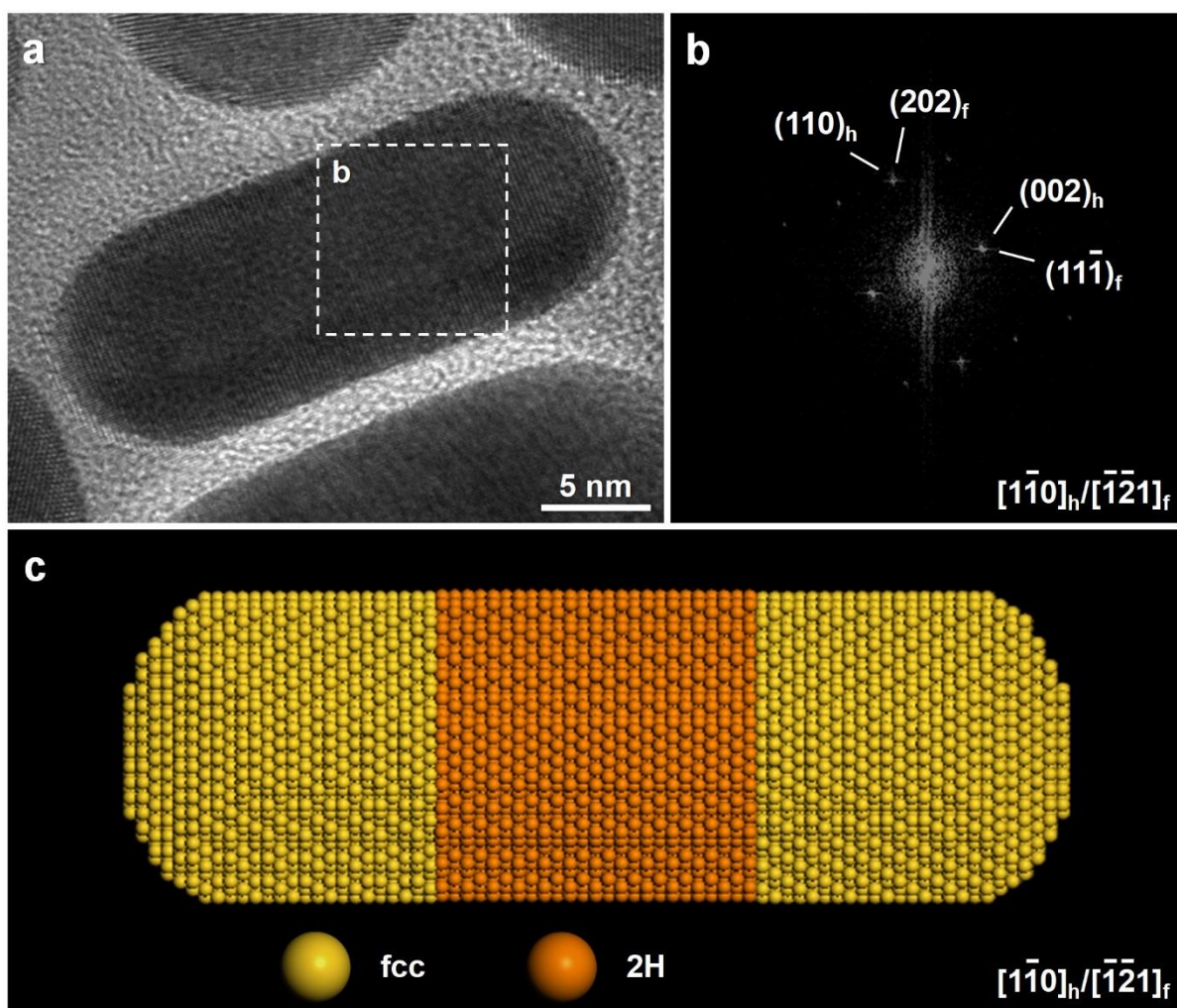
Supplementary Figure 4 | The effect of solvents. a-d, TEM images of Au nanostructures obtained by replacing the mixture of oleylamine and dodecylamine ($v/v = 2/3$) with (a) the pure oleylamine, (b) a mixture of oleylamine and octylamine ($v/v = 2/3$), (c) a mixture of oleylamine and hexylamine ($v/v = 2/3$), and (d) a mixture of oleylamine and dodecanol ($v/v = 2/3$).



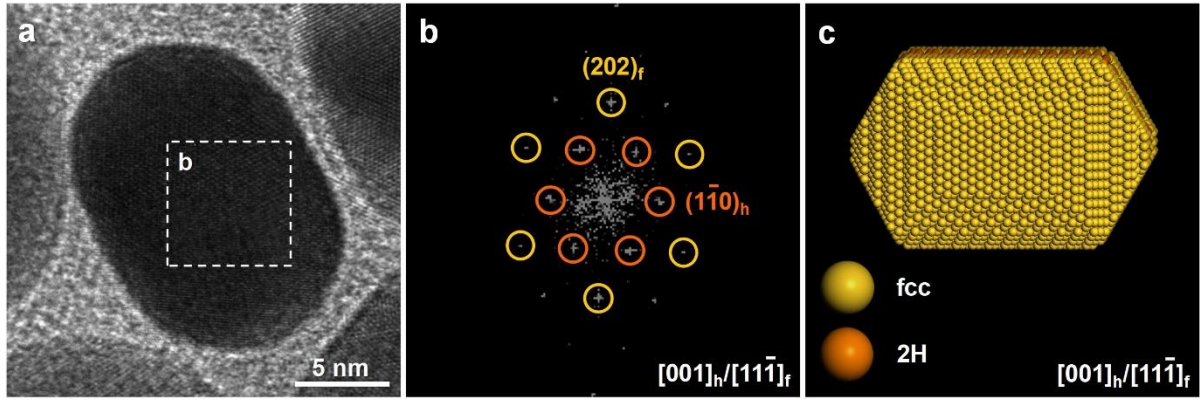
Supplementary Figure 5 | The effect of gas atmosphere. A typical TEM image of Au nanostructures obtained by changing the gas atmosphere from oxygen gas to air. The yellow arrows indicate the coexisting ultrathin Au nanowires, i.e., the by-product.



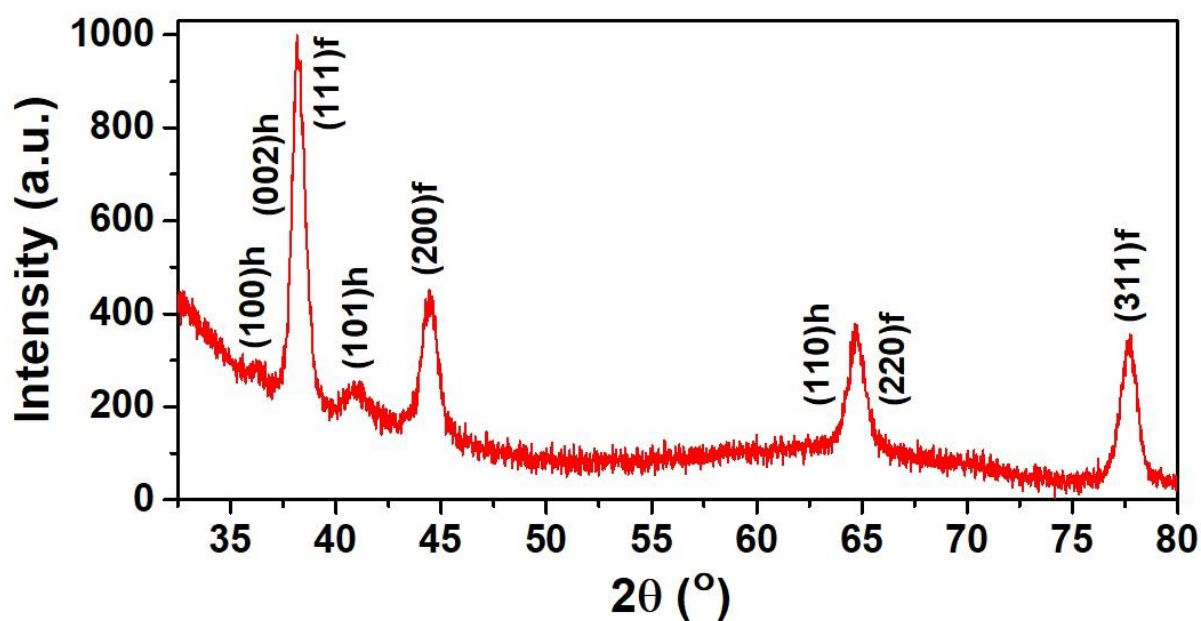
Supplementary Figure 6 | Schematic illustration for the view directions of fcc-2H-fcc Au NR. The atomic model of fcc-2H-fcc Au NR is taken from Fig. 1j. The X, Y and Z directions of Au NRs are parallel to the zone axes of $[110]_h/[101]_f$, $[1\bar{1}0]_h/[\bar{1}\bar{2}1]_f$ and $[001]_h/[11\bar{1}]_f$, respectively.



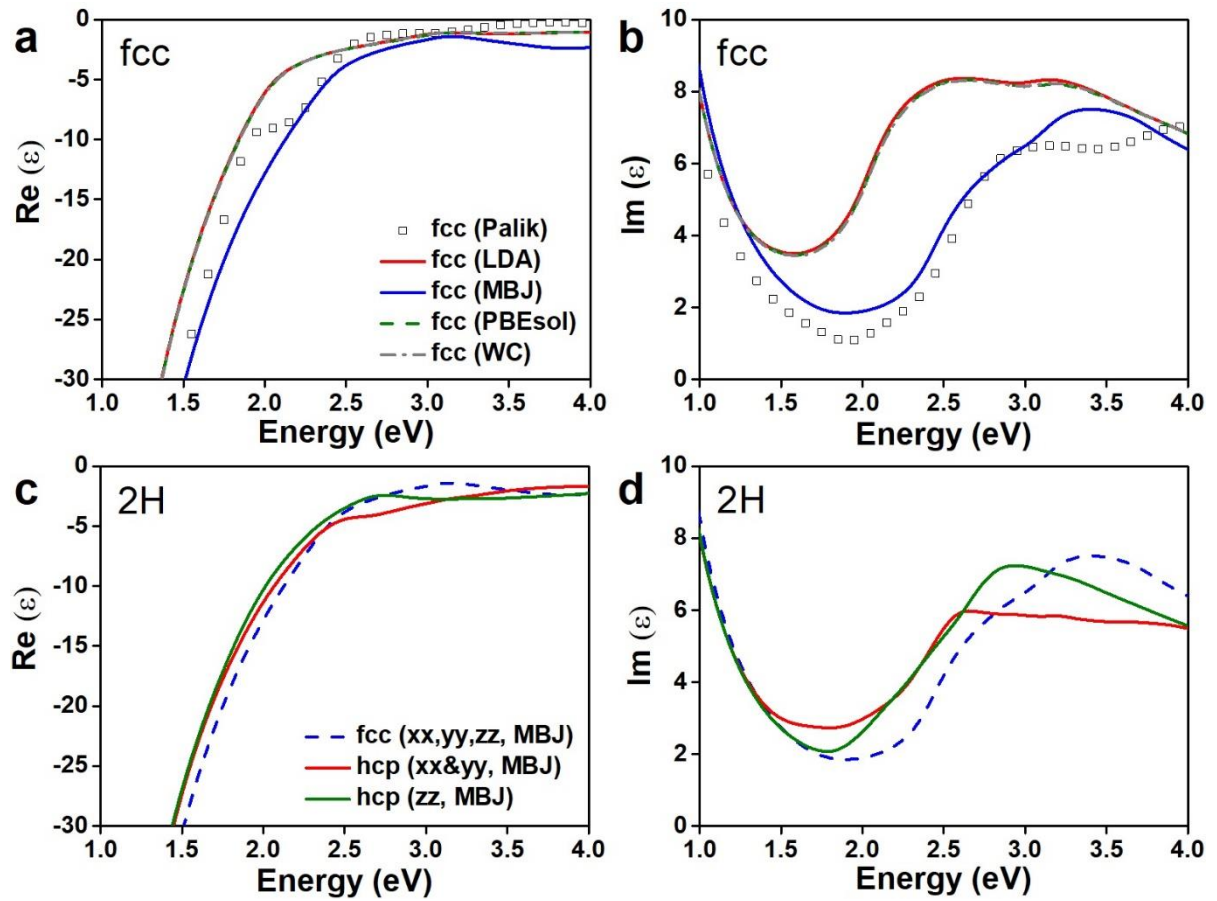
Supplementary Figure 7 | Structural characterization of fcc-2H-fcc Au NRs from the Y direction. **a**, HRTEM image taken from the Y direction of an Au NR. **b**, The corresponding FFT pattern of selected area in **a**, which matches well with the diffraction patterns of $[1\bar{1}0]_h$ and $[\bar{1}\bar{2}1]_f$ zone axes. **c**, An atomic model of the as-prepared heterophase fcc-2H-fcc Au NRs from the Y direction.



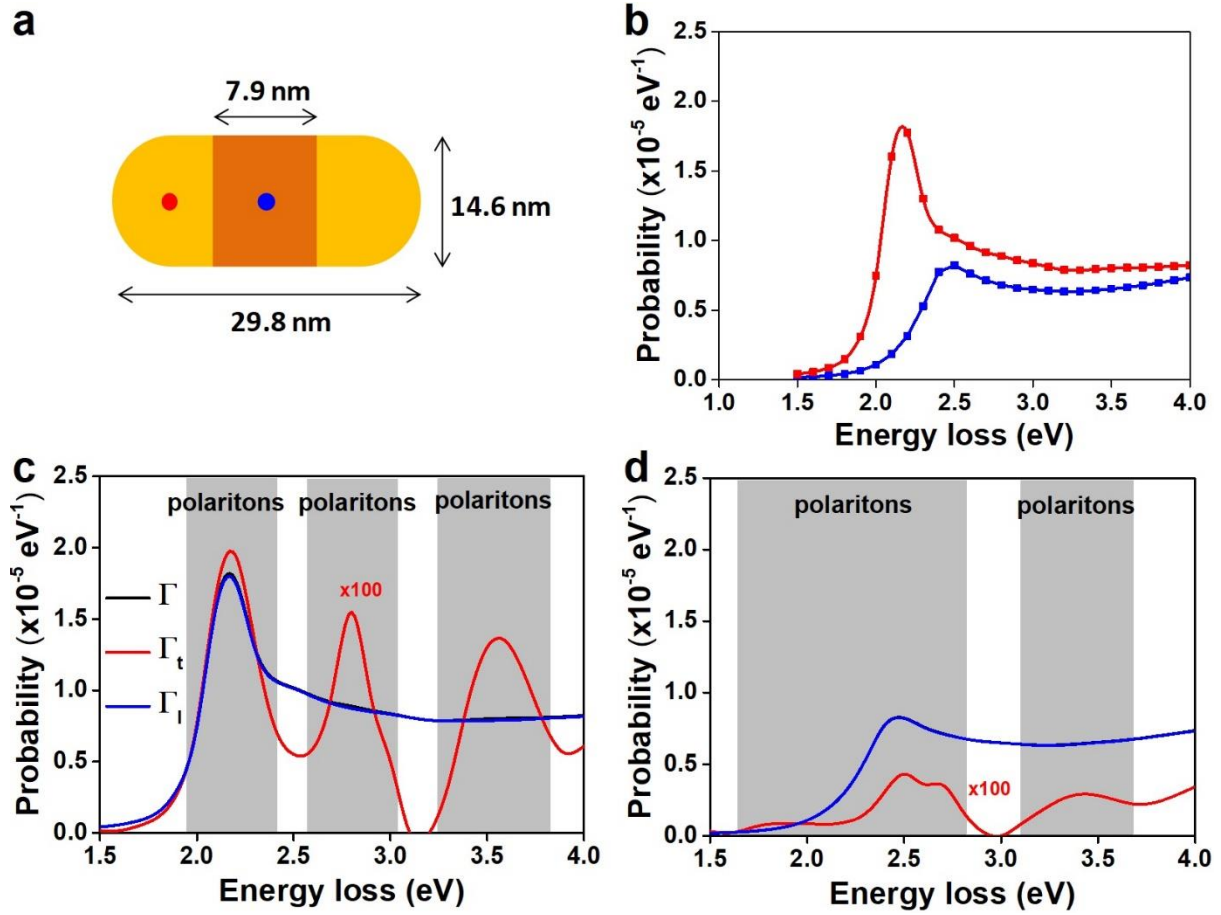
Supplementary Figure 8 | Structural characterization of fcc-2H-fcc Au NRs from the Z direction. **a**, HRTEM image taken from the Z direction of an Au NR. **b**, The corresponding FFT pattern of selected area in **a**, which shows two sets of diffraction spots belonging to the $(1\bar{1}0)_h$ and $(202)_f$ planes, respectively. It confirms the heterophase structure of the as-synthesized fcc-2H-fcc Au NRs. **c**, An atomic model of the as-prepared heterophase fcc-2H-fcc Au NRs from the Z direction.



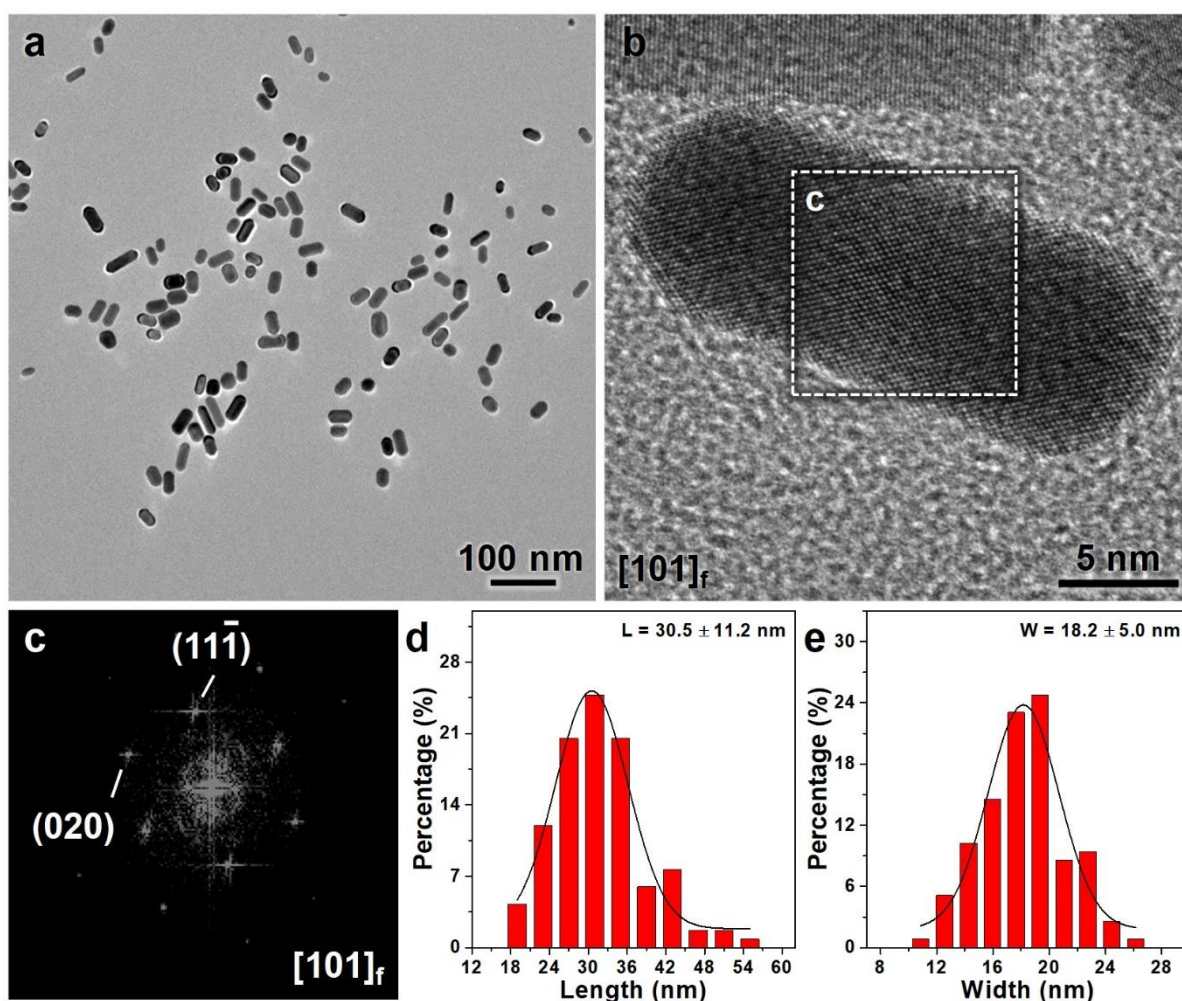
Supplementary Figure 9 | XRD characterization of fcc-2H-fcc Au NRs. The XRD pattern of fcc-2H-fcc Au NRs were collected in the $\theta/2\theta$ mode. Two sets of diffraction peaks belonging to 2H and fcc phases are observed, as indicated in the XRD pattern, which further confirms the fcc-2H-fcc heterophase structure of the obtained Au NRs.



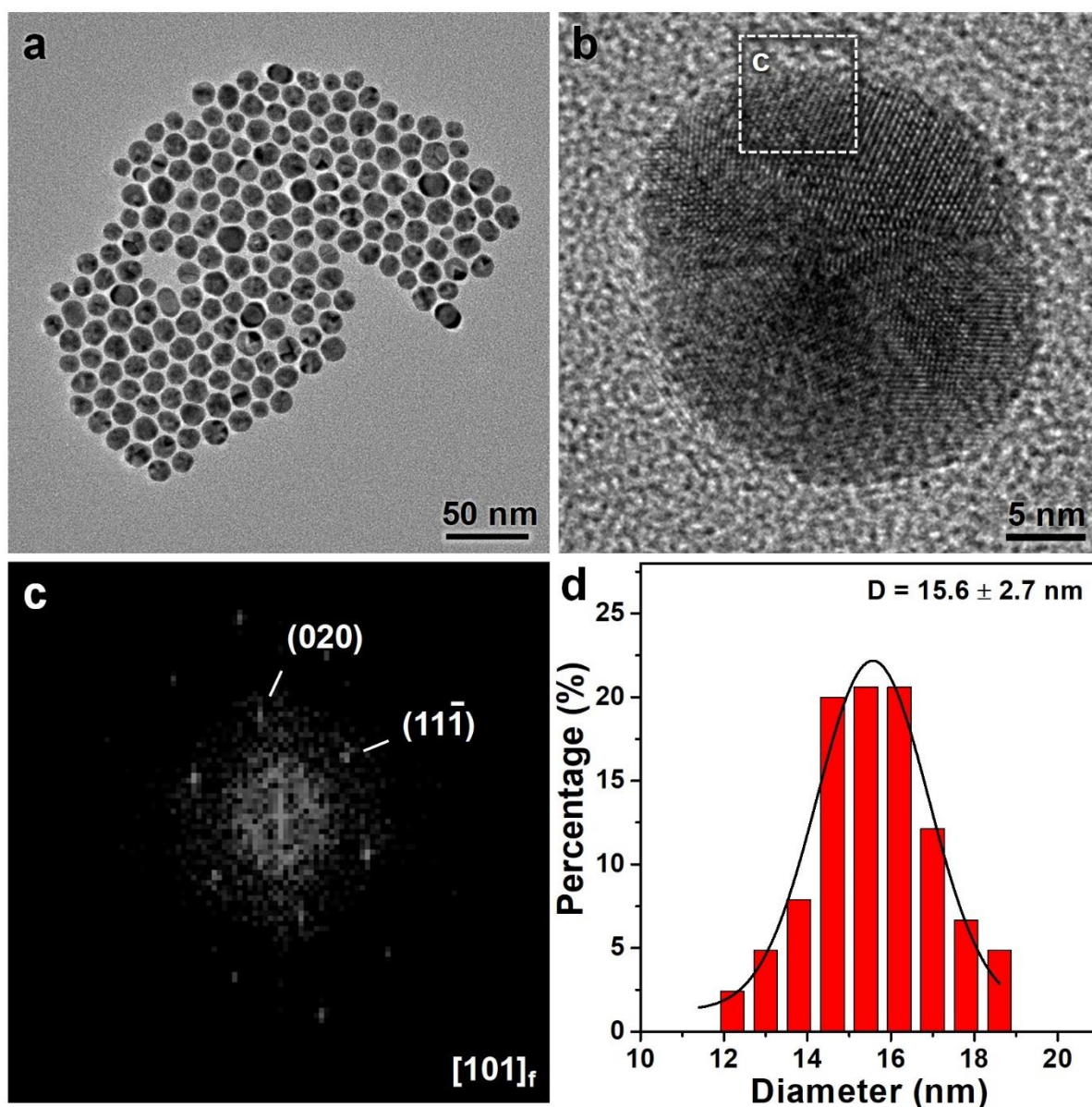
Supplementary Figure 10 | The calculations of dielectric permittivities for fcc Au and 2H Au. a-d, The computed complex dielectric permittivities of (a,b) fcc Au and (c,d) 2H Au using standard density functional theory (DFT) approaches. The computed functions for fcc Au are benchmarked against the experimentally measured permittivities from the Palik handbook (labeled as “Palik”). Note that the other abbreviations in this figure, i.e. “LDA”, “MBJ”, “PBEsol” and “WC”, stand for the “local density approximation”, “modified Becke-Johnson potential”, “revised Perdew-Burke-Ernzerh for solids generalized gradient approximation” and “Wu-Cohen generalized gradient approximation”, respectively.



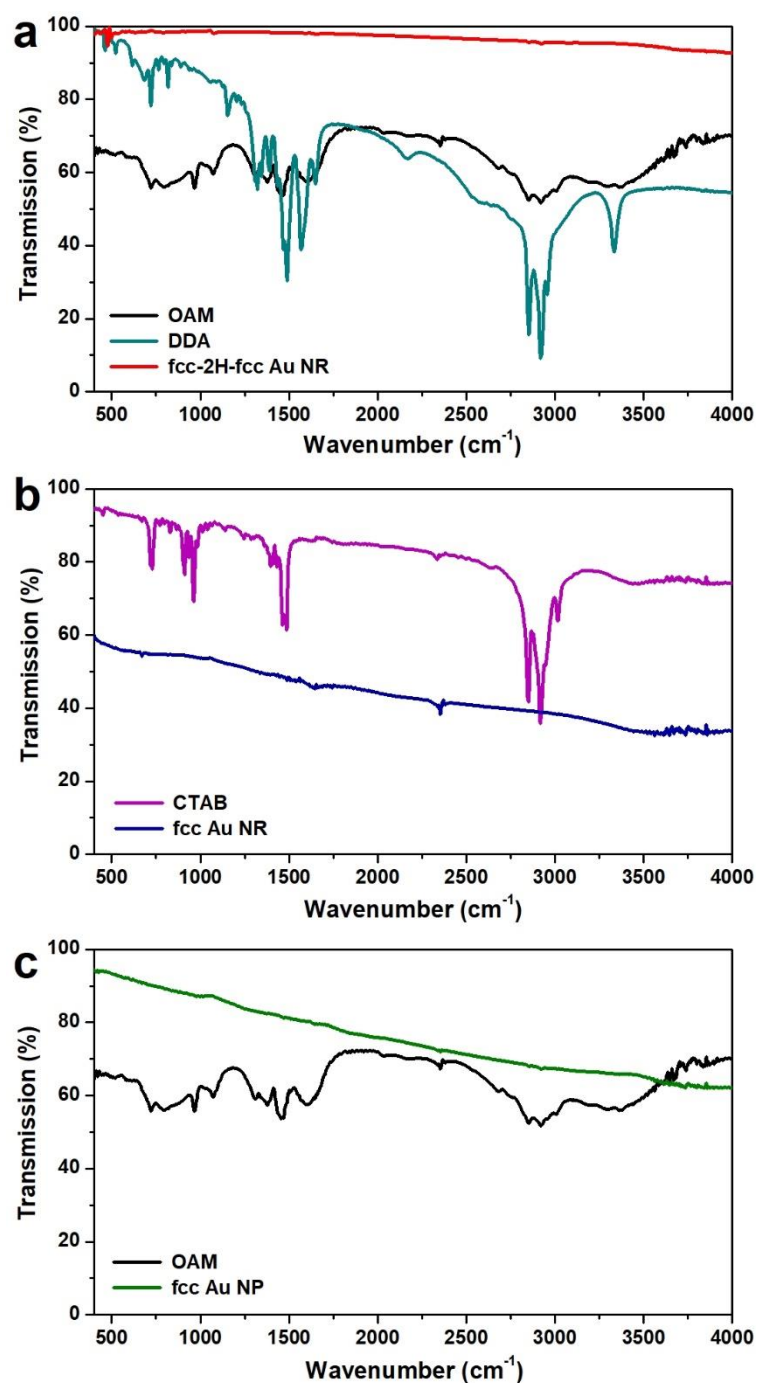
Supplementary Figure 11 | The Helmholtz decomposition of the EELS probability. **a**, The modelled heterophase fcc-2H-fcc Au NR. The model was built based on the Au NR shown in Fig. 2b. The length and width of the Au NR is 29.8 nm and 14.6 nm, respectively. The length of 2H phase in the middle of Au NR is measured to be 7.9 nm. **b**, The EELS spectra computed for two different positions of the E-beam shown by red and blue dots in **a**. **c,d**, Helmholtz decomposition of the EELS probability $\Gamma(\omega)$, which is obtained by locating the E-beam in the (c) end and (d) middle of Au NR, into loss contributions by transverse $\Gamma_t(\omega)$ and longitudinal $\Gamma_l(\omega)$ fields.



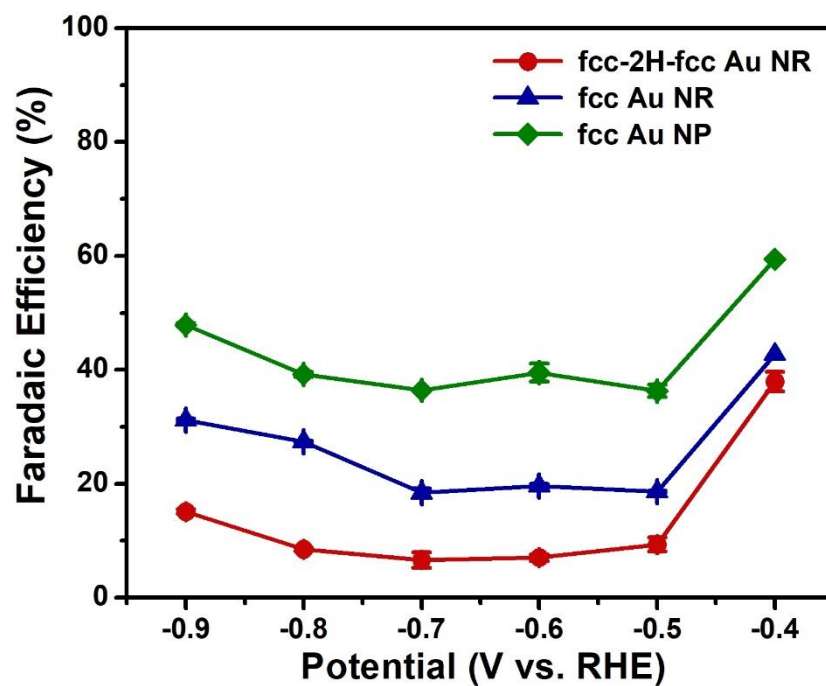
Supplementary Figure 12 | Structural characterization of fcc Au NRs. **a,b**, Low-magnification TEM (**a**) and HRTEM (**b**) images of fcc Au NRs. **c**, The corresponding FFT pattern of the selected area in **b**. **d**, Statistical analysis of the length of Au NRs measured by TEM, in which 30.5 nm is the average length and 11.2 nm is the standard deviation. **e**, Statistical analysis of the width of Au NRs measured by TEM, in which 18.2 nm is the average width and 5.0 nm is the standard deviation. The curves in **d** and **e** were obtained by fitting the data using a Gaussian function.



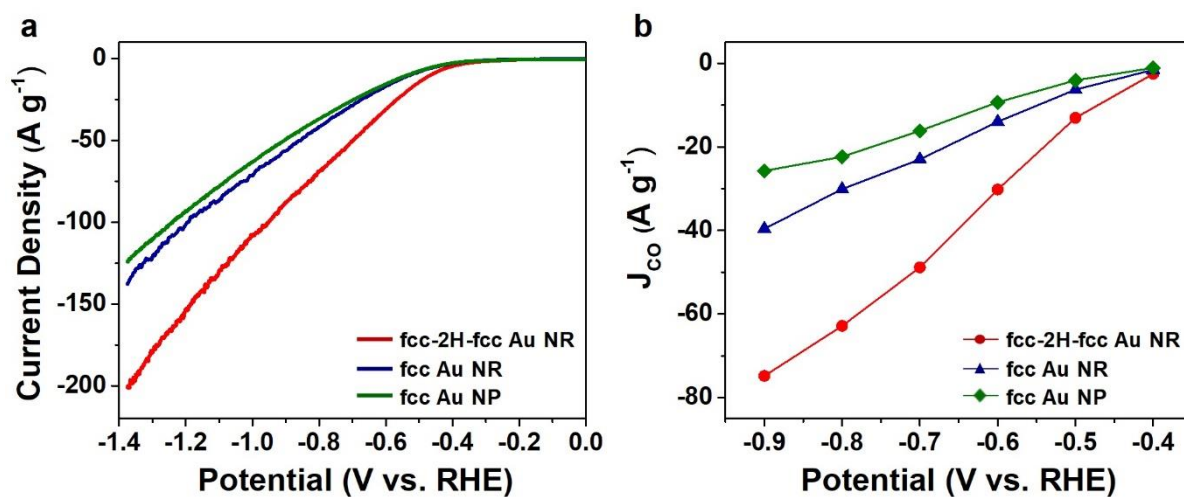
Supplementary Figure 13 | Structural characterization of fcc Au NPs. a,b, Low-magnification TEM (a) and HRTEM (b) images of fcc Au NPs. c, The corresponding FFT pattern of the selected area in b. d, Statistical analysis of the size of Au NPs measured by TEM, in which 15.6 nm is the average size and 2.7 nm is the standard deviation. The curve in d was obtained by fitting the data using a Gaussian function.



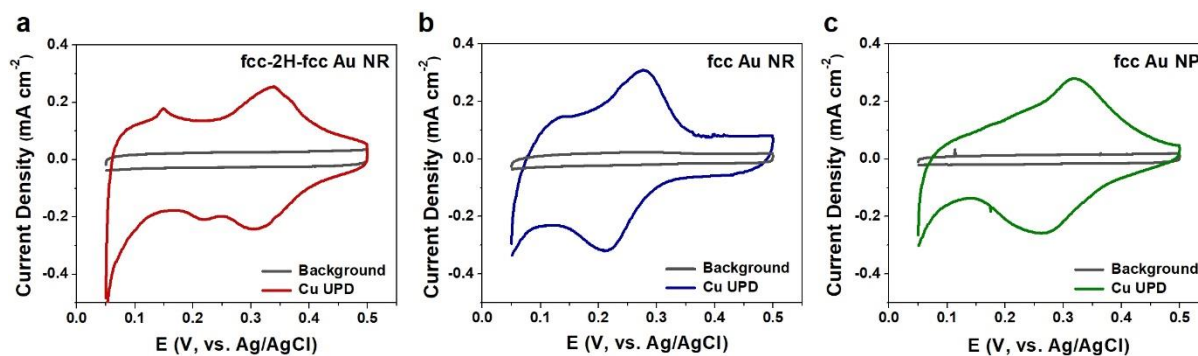
Supplementary Figure 14 | FTIR spectra of surface capping ligands and Au nanostructures after washing. **a**, FTIR spectra of oleylamine (OAM), dodecylamine (DDA) and the thoroughly washed fcc-2H-fcc Au NRs. **b**, FTIR spectra of cetyltrimethylammonium bromide (CTAB) and the thoroughly washed fcc Au NRs. **c**, FTIR spectra of OAM and the thoroughly washed fcc Au NPs. No obvious FTIR signals from surface capping ligands were observed after the Au nanostructures were thoroughly washed.



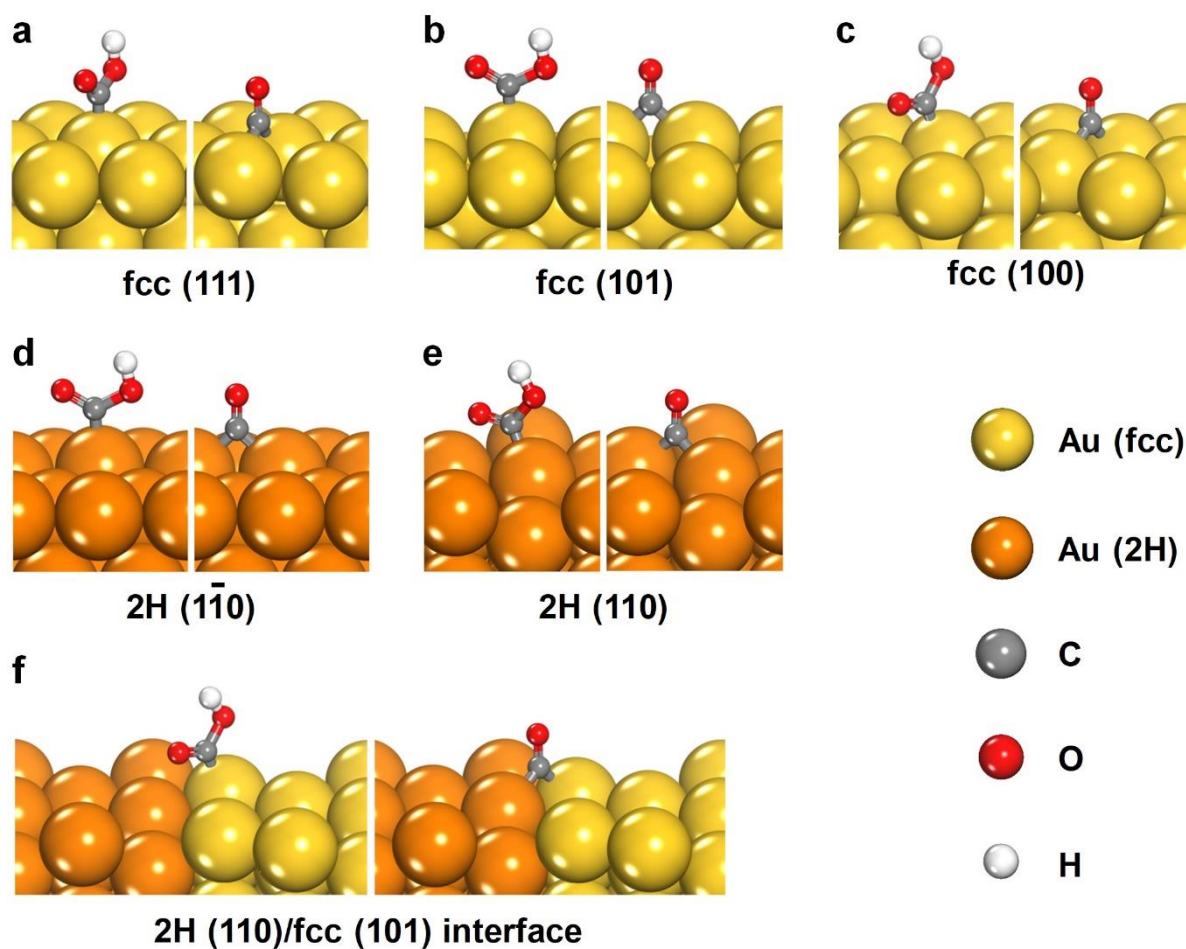
Supplementary Figure 15 | FEs of H₂. The FEs of H₂ for Au nanostructures, i.e. fcc-2H-fcc Au NRs, fcc Au NRs and fcc Au NPs at different applied potentials. Note that CO and H₂ are the only detectable products from the CO₂RR.



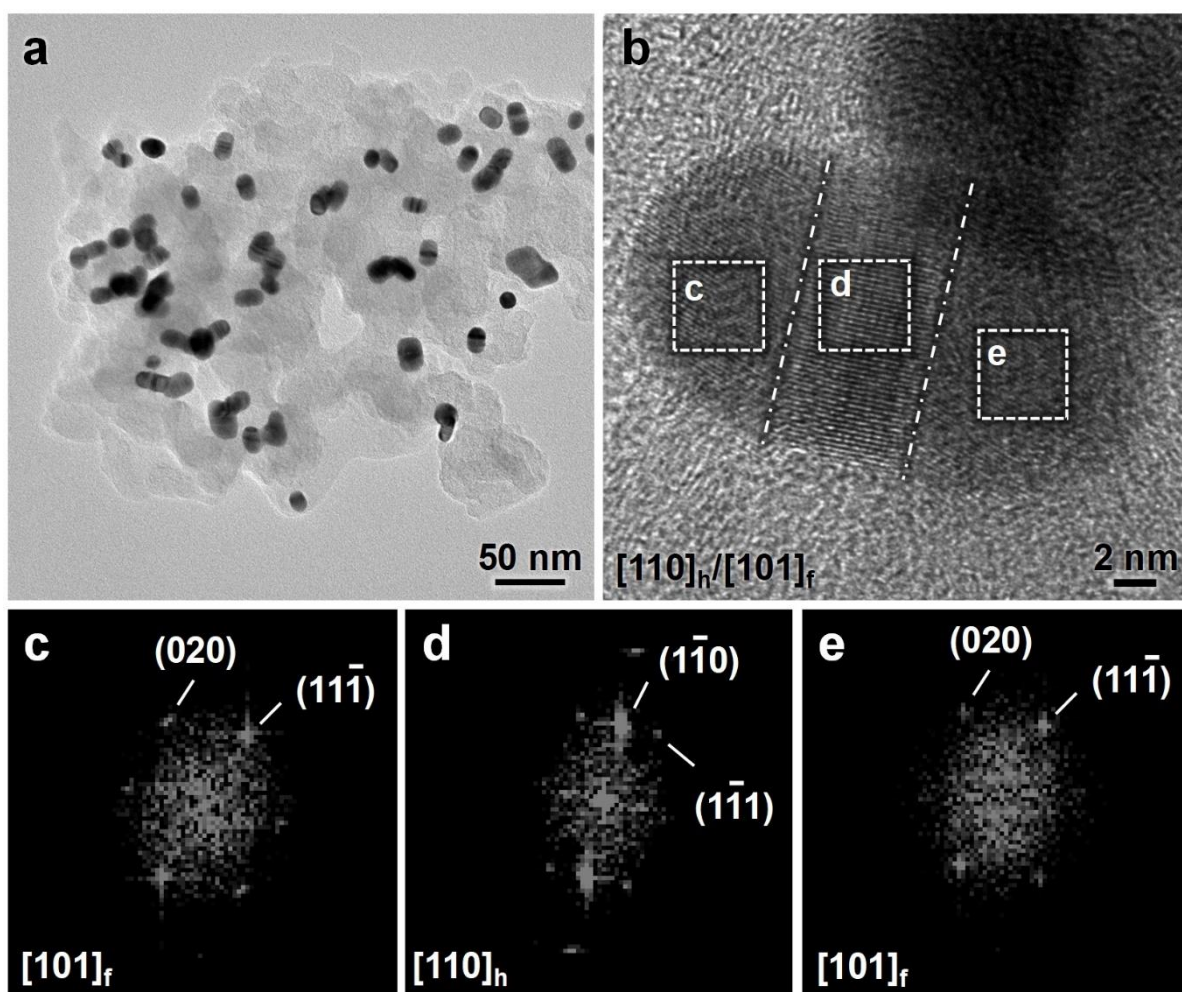
Supplementary Figure 16 | Mass activity. a,b, LSV curves (a) and CO partial current density (J_{CO}) (b) normalized by the mass of Au catalysts. Note that the total mass activity of fcc-2H-fcc Au NR is 30.8 A g^{-1} , and its partial mass activity for CO production is 30.2 A g^{-1} .



Supplementary Figure 17 | ECSA measurements. a-c, Cu underpotential deposition (UPD) and anodic stripping waves of (a) fcc-2H-fcc Au NR, (b) fcc Au NR and (c) fcc Au NP. The electrolyte solution is a mixture of CuSO_4 (0.1 M) and H_2SO_4 (0.5 M). The scan rate is 50 mV s^{-1} . ECSA was calculated by integrating the anodic peaks for Cu UPD stripping, and the baseline was determined in the absence of CuSO_4 .



Supplementary Figure 18 | Theoretical models. a-f, Atomic models of *COOH (left panels) and *CO (right panels) adsorbed on various surfaces, including (a) fcc (111), (b) fcc (101), (c) fcc (100), (d) 2H ($1\bar{1}0$), (e) 2H (110), and (f) 2H (110)/fcc (101) interface.



Supplementary Figure 19 | Structural characterization of fcc-2H-fcc Au NRs after the electrochemical durability measurement. **a,b**, TEM (**a**) and HRTEM (**b**) images of fcc-2H-fcc Au NRs after the stability test. The dashed-dotted white lines in **b** indicate the boundary between 2H and fcc phases. **c-e**, FFT patterns of the corresponding selected areas (**c,e**) in the two ends and (**d**) in the middle of the Au NR shown in **b**.

Supplementary Tables

Supplementary Table 1 | Comparison of catalytic performance of noble metal catalysts in CO₂RR towards CO production in previous reports and this work.

Catalysts	Electrolytes	FE at -0.6 V / %	Mass activity at -0.6 V / A g ⁻¹	Geometric current density at -0.6 V / mA cm ⁻²	Tafel slope / mV dec ⁻¹	Refs.
fcc-2H-fcc Au NR	0.5 M KHCO₃	98.2	30.8	8.18	64.9	This work
8 nm Au NP	0.5 M KHCO ₃	85	4.5	N. A.	N. A.	1
Ultrathin Au nanowire	0.5 M KHCO ₃	90	6.3	N. A.	N. A.	2
Grain boundary- rich Au NP	0.5 M NaHCO ₃	93	15	~ 0.9	N. A.	3
Au NP-CeO _x /C	0.1 M KHCO ₃	70	7	3.6	N. A.	4
Tetradentate porphyrin- capped Au NP	0.5 M KHCO ₃	93	N. A.	5.5	69	5
Thiolate-capped polycrystalline Au film	0.1 M KHCO ₃	~ 33	N. A.	N. A.	N. A.	6
Carbene- functionalized Au NP	0.1 M KHCO ₃	83	N. A.	~ 2	72	7
Au nanodendrite	0.2 M KHCO ₃	95	N. A.	2.5	69	8
Au needle film	0.5 M KHCO ₃	95	N. A.	80	42	9
Ag nanocoral film	0.1 M KHCO ₃	95	N.A.	6.9	58.5	10
Ag NP	0.5 M KHCO ₃	72	~ 8	~ 0.3	N. A.	11
Nanoporous Ag film	0.1 M KOH	90	N. A.	20	58	12
Triangular Ag nanoplates	0.1 M KHCO ₃	~ 55	N. A.	0.5	153	13
Plasma- activated Ag foil	0.1 M KHCO ₃	90	N. A.	2.5	N. A.	14

Oxide-derived Ag foil	0.2 M NaOH	80	N. A.	0.35	77	15
Oleylamine-Ag NP	0.5 M KHCO ₃	89	12 (at -0.65V)	N. A.	N. A.	16
Pd@Pd ₃ Au ₇ NP	0.5 M KHCO ₃	97	0.04	5	68.6	17
19.4 nm Pd icosahedra	0.1 M KHCO ₃	79	2.3	0.95	N. A.	18
3.7 nm Pd NP	0.1 M KHCO ₃	83	N. A.	~ 1.8	N. A.	19

Supplementary Table 2 | List of zero point energy (E_{ZPE}), entropy (S), enthalpic temperature (T) and correction to the solvation effect (G_{sol}) to gas or liquid phase molecules and adsorbed species. The unit for energy is eV.

Species	E_{ZPE}	TS	$\int C_p dT$	G_{sol}
CO₂ (g)	0.31	0.65	0.10	0.00
*COOH	0.62	0.18	0.09	-0.38
*CO	0.19	0.15	0.08	-0.10

Supplementary Notes

Supplementary Note 1

To investigate the effect of Au precursor in the synthesis of heterophase fcc-2H-fcc Au NRs, with the same molar concentration, HAuCl_4 , $\text{AuCl}_3 \cdot \text{Py}$, AuCl_3 , and $\text{Au}(\text{ac})_3$ were used to replace KAuCl_4 , respectively, and the other experimental conditions were kept same. When HAuCl_4 was used, various kinds of Au nanostructures, such as Au nanoplates, Au nanowires and 5-fold twinned Au nanoparticles, were obtained (Supplementary Fig. 3a). Similar results were also observed when the Au precursor was changed from KAuCl_4 to $\text{AuCl}_3 \cdot \text{Py}$ or AuCl_3 (Supplementary Fig. 3b,c). However, when KAuCl_4 was replaced with $\text{Au}(\text{ac})_3$, the obtained product was almost spherical Au nanoparticles (Supplementary Fig. 3d). The aforementioned experimental results indicate that the correct choice of Au precursor in our reaction is important for the successful synthesis of heterophase fcc-2H-fcc Au NRs.

Supplementary Note 2

To investigate the effect of solvent in the synthesis of heterophase fcc-2H-fcc Au NRs, the mixture of oleylamine and dodecylamine ($v/v = 2/3$) was replaced with the pure oleylamine, a mixture of oleylamine and octylamine ($v/v = 2/3$), a mixture of oleylamine and hexylamine ($v/v = 2/3$), and a mixture of oleylamine and dodecanol ($v/v = 2/3$), respectively, and the other experimental conditions were kept same. When the pure oleylamine was used as the solvent, irregular-shaped Au nanoparticles were obtained (Supplementary Fig. 4a). When the mixture of oleylamine and octylamine or the mixture of oleylamine and hexylamine was used as the solvent, spherical Au nanoparticles were obtained (Supplementary Fig. 4b,c). Moreover, when the mixture of oleylamine and dodecanol was used as the solvent, spherical Au nanoparticles together with little amount of Au nanorods were obtained (Supplementary Fig. 4d). The aforementioned experimental results indicate that the correct choice of solvent in the reaction is important for the successful synthesis of heterophase fcc-2H-fcc Au NRs.

Supplementary Note 3

To investigate the effect of gas atmosphere in the synthesis of heterophase fcc-2H-fcc Au NRs, air was used to replace the oxygen gas, and the other experimental conditions were kept same. When the reaction was conducted in air, besides non-uniform Au nanorods with large size distribution, irregular-shaped Au nanostructures and ultrathin Au nanowires were also obtained (Supplementary Fig. 5), indicating that the correct choice of gas atmosphere in the reaction is important for the successful synthesis of heterophase fcc-2H-fcc Au NRs.

Supplementary References

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