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Mono-, di- and trimetallic coinage nanoparticles prepared via the Brust–Schiffrin method

Hongmei Liu*, Yuting Li, Tian Li, Yunyun Mu, Xiaohui Fang and Xinping Zhang*

Institute of Information Photonics Technology, School of Physics and Optoelectronic Engineering, Beijing University of Technology, Beijing 100124, P. R. China
**E-mail: hmliu@bjut.edu.cn, zhangxinping@bjut.edu.cn*

S1 Synthesis of Ag, Cu and Au mono metallic nanoparticles (NPs) by the Brust-Schiffrin method

S1.1 Synthesis of Ag nanoparticles

We dissolved TOAB (1.5 g, 2.74 mmol) in 80 ml toluene and stirred until it had completely dissolved. Then, $AgNO_3$ (0.13 g, 0.78 mmol) in 5 mL of water was added, and then NaBr (0.32 g, 3.12 mmol) was added. Continue stirring until the pale-yellow AgBr precipitate disappeared, and both the organic phase and the aqueous phase became colorless and transparent. Then 1-hexanethiol (0.37 g, 3.12 mmol) was added to the solution. After stirring for 10 minutes, 20 mL of freshly prepared aqueous $NaBH_4$ (0.28 g, 7.4 mmol) was quickly poured into the flask and the solution immediately turned dark. The organic phase was collected after 4 h of reaction and the organic solvent was removed using a rotary evaporator at a temperature below 50 °C. The remaining black muddy product was suspended in 30 mL of methanol, briefly sonicated to ensure complete dissolution of byproducts, collected by centrifugation (8000 rpm for 5 min), and then washed five times with 20 mL of methanol. Upon drying at room temperature under vacuum, the black powder of Ag NPs was obtained.

In this synthesis process, 4 equivalents of 1-hexanethiol were used, and the corresponding reaction equations are as follows:

$$\mathrm{TOAB} \rightarrow [\mathrm{TOA}]^{+} + \mathrm{Br}^{-} \tag{1}$$

$$\mathrm{AgNO_3} + \mathrm{Br}^{-} \rightarrow \mathrm{AgBr}\downarrow + \mathrm{NO_3}^{-} \tag{2}$$

$$\mathrm{AgBr} + \mathrm{Br}^{-} + \mathrm{TOAB} \rightarrow [\mathrm{TOA}][\mathrm{Ag(I)Br_2}] \tag{3}$$

$$[\mathrm{TOA}][\mathrm{Ag(I)Br_2}] + 2\mathrm{RSH} \rightarrow [\mathrm{TOA}][\mathrm{Ag(I)\,SR_2}] + 2\mathrm{HBr} \tag{4}$$

$$\mathrm{NaBH_4} \rightarrow \mathrm{Na}^{+} + \mathrm{BH_4}^{-} \tag{5}$$

$$[\mathrm{TOA}] + 3\mathrm{H_2O} + \mathrm{BH_4}^{-} \rightarrow \mathrm{B(OH)_3} + 3\mathrm{H_2}\uparrow + [\mathrm{TOA}]\mathrm{H} \tag{6}$$

$$[\mathrm{TOA}][\mathrm{Ag(I)\,SR_2}] + [\mathrm{TOA}]\mathrm{H} \rightarrow [\mathrm{TOA}][\mathrm{H\text{-}Ag(I)\text{-}SR}] + \mathrm{TOASR} \tag{7}$$

n[TOA][H-Ag(I)-SR] + m[TOA][Ag(I) SR_2] → thiolate-protected Ag(I) hydride clusters → Ag NPs (8)

S1.2 Synthesis of Au nanoparticles

We dissolved TOAB (1.5 g, 2.74 mmol) in 80 ml toluene and stirred until it had completely dissolved. Then, $HAuCl_4 \cdot 4H_2O$ (0.32 g, 0.78 mmol) in 5 mL of water was added. The organic phase became red-brown, and simultaneously, the yellow aqueous phase became colorless. After 1-hexanethiol (0.37g, 3.12 mmol) was added to the solution, after which the organic phase quickly became colorless. After stirring for 10 minutes, 20 mL of freshly prepared aqueous $NaBH_4$ (0.28 g, 7.4 mmol) was quickly poured into the flask and the solution immediately turned dark. The organic phase was collected after 4 h of reaction and the organic solvent was removed using a rotary evaporator at temperature below 50 °C. The remaining black muddy product was suspended in 30 mL of methanol, briefly sonicated to ensure complete dissolution of byproducts, collected by a centrifugation (8000 rpm for 5 min), and then washed five times with 20 mL of methanol. Upon drying at room temperature under vacuum, the black powder of Au NPs was obtained.

In this synthesis process, 4 equivalents of 1-hexanethiol were used, and the corresponding reaction equations are as follows:

$\mathrm{TOAB} \rightarrow [\mathrm{TOA}]^+ + \mathrm{Br}^-$ (1)

$\mathrm{HAu(III)Cl_4} \rightarrow [\mathrm{Au(III)Cl_4}]^- + \mathrm{H}^+$ (2)

$[\mathrm{TOA}]^+ + [\mathrm{Au(III)Cl_4}]^- \rightarrow [\mathrm{TOA}][\mathrm{Au(III)Cl_4}] + \mathrm{Cl}^-$ (3)

$[\mathrm{TOA}][\mathrm{Au(III)Cl_4}] + 6\mathrm{TOAB} \rightarrow [\mathrm{TOA}][\mathrm{Au(III)Br_4}] + 4[\mathrm{TOA}]\mathrm{Cl}$ (4)

$[\mathrm{TOA}][\mathrm{Au(III)Br_4}] + 2\mathrm{RSH} \rightarrow [\mathrm{TOA}][\mathrm{Au(I)\,Br_2}] + \mathrm{RS\text{-}SR} + 2\mathrm{HBr}$ (5)

$[\mathrm{TOA}][\mathrm{Au(I)Br_2}] + 2\mathrm{RSH} \rightarrow [\mathrm{TOA}][\mathrm{Au(I)\,SR_2}] + 2\mathrm{HBr}$ (6)

$\mathrm{NaBH_4} \rightarrow \mathrm{Na}^+ + \mathrm{BH_4}^-$ (7)

$[\mathrm{TOA}]^+ + 3\mathrm{H_2O} + \mathrm{BH_4}^- \rightarrow \mathrm{B(OH)_3} + 3\mathrm{H_2}\uparrow + [\mathrm{TOA}]\mathrm{H}$ (8)

$[\mathrm{TOA}][\mathrm{Au(I)\,(SR)_2}] + [\mathrm{TOA}]\mathrm{H} \rightarrow [\mathrm{TOA}][\mathrm{H\text{-}Au(I)\text{-}SR}] + [\mathrm{TOA}]\mathrm{SR}$ (9)

n[TOA][H-Au(I)-SR] + m[TOA][Au(I) $(SR)_2$]→ thiolate-protected Au(I) hydride clusters → Au NPs (10)

S1.3 Synthesis of the NPs of Cu(I) -thiolates

We dissolved TOAB (1.5 g, 2.74 mmol) in 80 ml toluene and stirred until it had completely dissolved. Then, $CuBr_2$ (0.174 g, 0.78 mmol) and NaBr (0.64 g, 6.24 mmol) in 5 mL of water was added. The organic phase became yellow, then quickly changed to purple and dark purple. Simultaneously, the blue aqueous phase became light blue. After stirring for 10 min, 1-hexanethiol (0.37 g, 3.12 mmol) was added to the solution, after which the organic phase quickly became colorless. At the same time, the light blue aqueous phase became colorless. After stirring for another 10 minutes, 20 mL of freshly prepared aqueous $NaBH_4$ (0.28 g, 7.4 mmol) was quickly poured into the flask and the solution immediately turned to red-brown. The organic phase was collected after 4 h of reaction and the organic solvent was removed using a rotary evaporator at a temperature below 50 °C. The remaining black muddy product was suspended in 30 mL of methanol, briefly sonicated to ensure complete dissolution of by-products, collected by centrifugation (8000 rpm for 5 min), and then washed five times with 20 mL of methanol. Upon drying at room temperature under vacuum, the yellow powder of Cu(I)-thiolates was obtained.

In this synthesis process, 4 equivalents of 1-hexanethiol were used, and the corresponding reaction equations are as follows:

$\mathrm{TOAB} \rightarrow [\mathrm{TOA}]^+ + \mathrm{Br}^-$ (1)

$\mathrm{CuBr_2} + \mathrm{H_2O} + \mathrm{Br}^- \rightarrow [\mathrm{Cu(II)(H_2O)_4}]^{2+}$ (2)

$[\mathrm{Cu(II)(H_2O)_4}]^{2+} + \mathrm{Br}^- \rightarrow [\mathrm{Cu(II)(H_2O)_3Br}]^+ + \mathrm{H_2O}$ (3)

$[\mathrm{Cu(II)(H_2O)_3Br}]^+ + \mathrm{Br}^- \rightarrow [\mathrm{Cu(II)(H_2O)_2Br_2}] + \mathrm{H_2O}$ (4)

$[\mathrm{Cu(II)(H_2O)_2Br_2}] + \mathrm{Br}^- \rightarrow [\mathrm{Cu(II)(H_2O)Br_3}]^- + \mathrm{H_2O}$ (5)

$[\mathrm{TOA}]^+ + [\mathrm{Cu(II)(H_2O)Br_3}]^- \rightarrow [\mathrm{TOA}][\mathrm{Cu(II)(H_2O)Br_3}]$ (yellow) (6)

$[\mathrm{TOA}][\mathrm{Cu(II)(H_2O)Br_3}] + \mathrm{TOAB} \rightarrow [\mathrm{TOA}]_2[\mathrm{Cu(II)Br_4}]$ (purple) $+ \mathrm{H_2O}$ (7)

$2[\mathrm{TOA}]_2[\mathrm{Cu(II)Br_4}] + 2\mathrm{RSH} \rightarrow 2[\mathrm{TOA}][\mathrm{Cu(I)Br_2}] + \mathrm{RS\text{-}SR} + 2\mathrm{HBr} + 2\mathrm{TOAB}$ (8)

$[\mathrm{TOA}][\mathrm{Cu(I)Br_2}] + 2\mathrm{RSH} \rightarrow [\mathrm{TOA}][\mathrm{Cu(I)\,SR_2}] + 2\mathrm{HBr}$ (9)

$\mathrm{NaBH_4} \rightarrow \mathrm{Na}^+ + \mathrm{BH_4}^-$ (10)

$[\mathrm{TOA}]^+ + 3\mathrm{H_2O} + \mathrm{BH_4}^- \rightarrow \mathrm{B(OH)_3} + 3\mathrm{H_2}\uparrow + [\mathrm{TOA}]\mathrm{H}$ (11)

$[\mathrm{TOA}][\mathrm{Cu(I)\,SR_2}] + [\mathrm{TOA}]\mathrm{H} \rightarrow [\mathrm{TOA}][\mathrm{H\text{-}Cu(I)\text{-}SR}]$ (12)

$n[\mathrm{TOA}][\mathrm{H\text{-}Cu(I)\text{-}SR}] + m[\mathrm{TOA}][\mathrm{Cu(I)\,SR_2}] \rightarrow$ thiolate-protected Cu(I) hydride clusters → Cu(I)-thiolates (13)

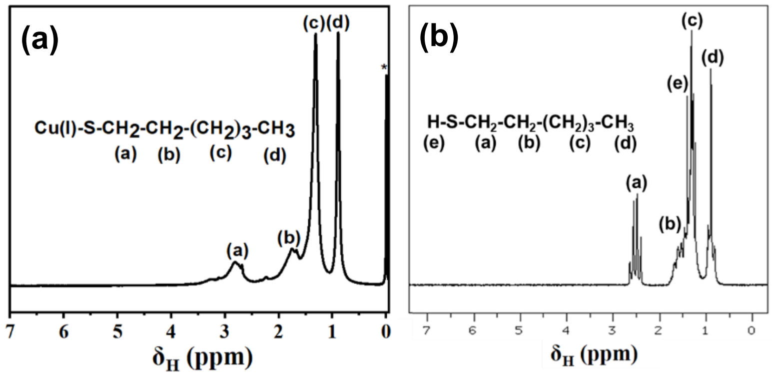


Fig. S1 ^{1}H NMR spectrum of (a) Cu products synthesized using 4 equiv of 1-hexanethiol and (b) pure 1-hexanethiol solution from the reagent company.

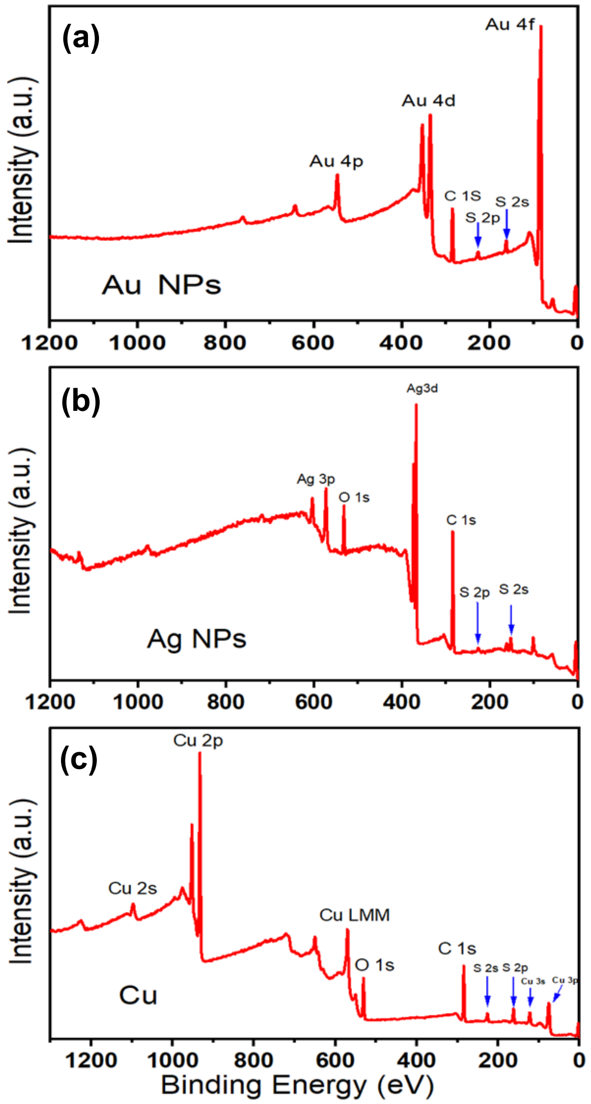


Fig. S2 The XPS survey spectrum of (a)Au NPs, (b)Ag NPs and (c) Cu(I) nanoclusters synthesized using 4 equiv of 1-hexanethiol.

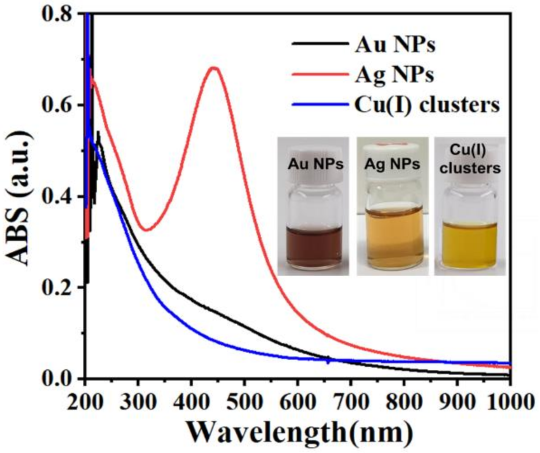


Fig. S3 UV-vis absorption spectra of Au, Ag and Cu monometallic products dispersed in n-hexane.

S1.4 Synthesis of Cu nanoparticles

We dissolved TOAB (1.5 g, 2.74 mmol) in 80 ml toluene and stirred until it had completely dissolved. Then, $CuBr_2$ (0.174 g, 0.78 mmol) and NaBr (0.64 g, 6.24 mmol) in 5 mL of water was added. The organic phase became yellow, then quickly changed to purple and dark purple. Simultaneously, the blue aqueous phase became light blue. After stirring for 10 min, 1-hexanethiol (0.09 g, 0.78 mmol) was added to the solution, after which the organic phase quickly became light yellow. At the same time, the light blue aqueous phase became colorless. After stirring for another 10 minutes, 20 mL of freshly prepared aqueous $NaBH_4$ (0.28 g, 7.4 mmol) was quickly poured into the flask and the solution gradually turned to brown, then brown-black. The organic phase was collected after 4 h of reaction and the organic solvent was removed using a rotary evaporator at a temperature below 50 °C. The remaining black muddy product was suspended in 30 mL of methanol, briefly sonicated to ensure complete dissolution of byproducts, collected by centrifugation (8000 rpm for 5 min), and then washed 5 times with 20 mL of methanol. Upon drying at room temperature under vacuum, the black powder of Cu NPs was obtained.

In this synthesis process, 1 equivalent of 1-hexanethiol was used, and the corresponding reaction equations are as follows:

$$\mathrm{TOAB} \rightarrow [\mathrm{TOA}]^{+} + \mathrm{Br}^{-} \quad (1)$$

$$\mathrm{CuBr_2} + \mathrm{H_2O} + \mathrm{Br}^{-} \rightarrow [\mathrm{Cu(II)(H_2O)_4}]^{2+} \quad (2)$$

$$[\mathrm{Cu(II)(H_2O)_4}]^{2+} + \mathrm{Br}^{-} \rightarrow [\mathrm{Cu(II)(H_2O)_3Br}]^{+} + \mathrm{H_2O} \quad (3)$$

$$[\mathrm{Cu(II)(H_2O)_3Br}]^{+} + \mathrm{Br}^{-} \rightarrow [\mathrm{Cu(II)(H_2O)_2Br_2}] + \mathrm{H_2O} \quad (4)$$

$[Cu(II)(H_2O)_2Br_2] + Br^- \rightarrow [Cu(II)(H_2O)Br_3]^- + H_2O$ (5)

$[TOA]^+ + [Cu(II)(H_2O)Br_3]^- \rightarrow [TOA][Cu(II)(H_2O)Br_3]$ (yellow) (6)

$[TOA][Cu(II)(H_2O)Br_3] + TOAB \rightarrow [TOA]_2[Cu(II)Br_4]$ (purple) $+H_2O$ (7)

$2[TOA]_2[Cu(II)Br_4] + 2RSH \rightarrow 2[TOA][Cu(I)Br_2] + RS\text{-}SR + 2HBr + 2TOAB$ (8)

$NaBH_4 \rightarrow Na^+ + BH_4^-$ (9)

$[TOA]^+ + 3H_2O + BH_4^- \rightarrow B(OH)_3 + 3H_2\uparrow + [TOA]H$ (10)

$[TOA][Cu(I)Br_2] + [TOA]H \rightarrow [TOA][H\text{-}Cu(I)\text{-}Br]$ (11)

$n[TOA][H\text{-}Cu(I)\text{-}Br] + m[TOA][Cu(I)Br_2] \rightarrow Br^-$ protected Cu(I) hydride clusters $\rightarrow Br^-$ protected Cu(0) NPs (12)

$RSSR + 2[TOA]H \rightarrow 2RSH$ (13)

Br^- protected Cu(0) NPs + RSH → thiolate-protected Cu(0) NPs + HBr (14)

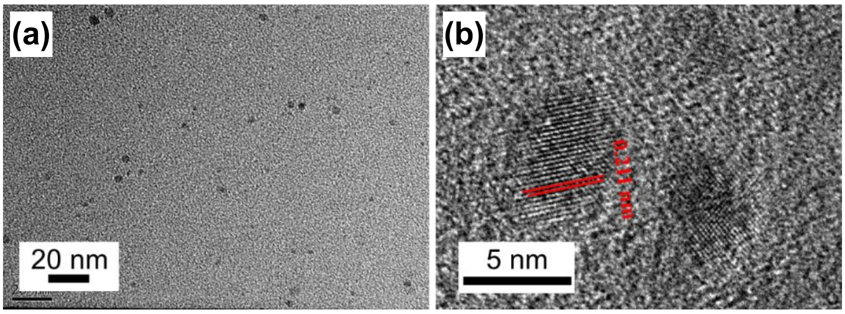


Fig. S4 (a) TEM images of Cu NPs synthesized using 1 equiv of 1-hexanethiol and (b) HRTEM image of Cu NPs.

S2 Synthesis of Au_1Ag_1 bimetallic nanoparticles by the Brust-Schiffrin method

We dissolved TOAB (1.5 g, 2.74 mmol) in 80 ml toluene and stirred until TOAB it had completely dissolved. Then, $AgNO_3$ (0.066 g, 0.39 mmol) in 5 mL of water was added, and then NaCl (0.18 g, 3.12 mmol) was added. Continue stirring until the white AgCl precipitate disappeared, and both the organic phase and the aqueous phase became colorless and transparent. Then, $HAuCl_4{\cdot}4H_2O$ (0.16 g, 0.39 mmol) in 2 mL of water was added to the flask and the organic phase became deep reddish brown. After stirring for 10 min, 1-hexanethiol (0.37 g, 3.12 mmol) was added to the solution, after which the organic phase became colorless. After stirring for another 10 minutes, quickly poured 20 mL of freshly prepared aqueous $NaBH_4$ (0.28 g, 7.4 mmol) into the flask and the solution quickly turned dark. The organic phase was collected after 4 h of reaction and the organic solvent was removed using a rotary evaporator at a temperature below 50°C. The remaining black muddy product was suspended in 30 mL of methanol, briefly sonicated to ensure complete dissolution of byproducts, collected by centrifugation (8000 rpm for 5 min), and then washed five times with 20 mL of methanol. Upon drying at room temperature under vacuum, the black powder with an Au to Ag mole ratio of 1:1 was obtained. By changing the stoichiometry of silver nitrate and gold chloride, the NPs with different Au and Ag molar ratio can be obtained.

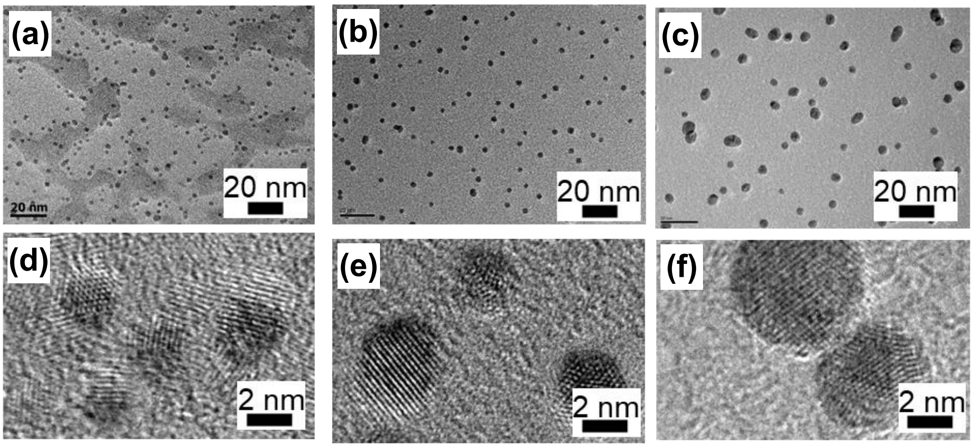


Fig. S5 TEM and high-resolution TEM images of Au–Ag alloy nanoparticles with different Au/Ag molar ratios: (a, d) Au_1Ag_2; (b, e) Au_1Ag_8 and (c, f) Ag.

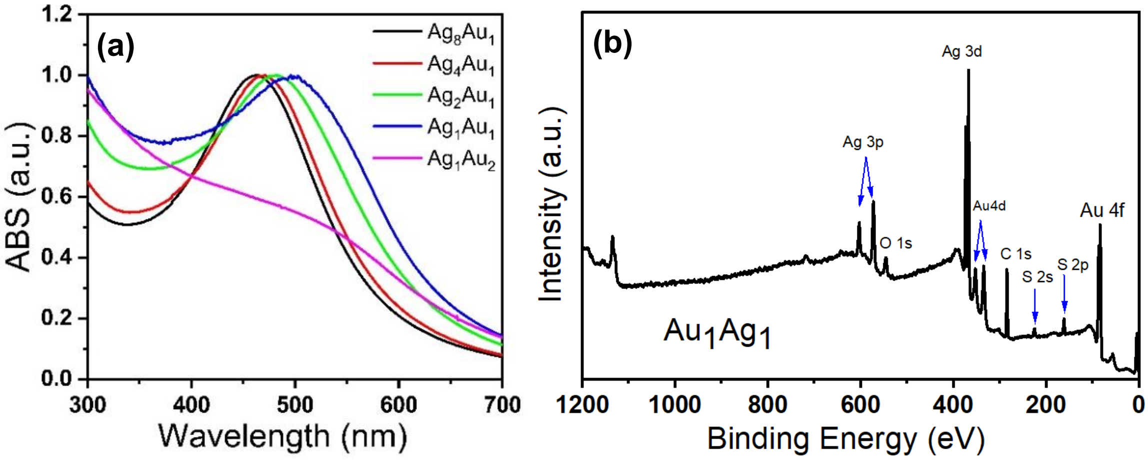


Fig. S6 (a) UV-vis absorption spectra of Au-Ag bimetallic NPs with various atomic fractions dispersed in n-hexane, (b) The XPS survey spectrum of Au_1Ag_1 bimetallic NPs.

S3 Synthesis of Au_1Cu_1 bimetallic nanoparticles by the Brust-Schiffrin method

We dissolved TOAB (1.5 g, 2.74 mmol) in 80 ml toluene and stirred until it had completely dissolved. Then, $CuBr_2$ (0.087 g, 0.39 mmol) and NaBr (0.64 g, 6.24 mmol) in 5 mL of water was added. The organic phase firstly became yellow, then changed to purple and then dark purple. Continue stirring until the aqueous phase turn from blue to colorless. Then $HAuCl_4\cdot 4H_2O$ (0.16 g, 0.39 mmol) in 2 mL of water was added to the flask. After stirring for 10 min, add 1-hexanethiol (0.37g, 3.12 mmol) to the solution, the organic phase became colorless. After stirring for another 10 minutes, quickly poured 20 mL of freshly prepared aqueous $NaBH_4$ (0.28 g, 7.4 mmol) into the flask and the solution quickly turned dark. The organic phase was collected after 4 h of reaction and the organic solvent was removed using a rotary evaporator at a temperature below 50 °C. The remaining black muddy product was suspended in 30 mL of methanol, briefly sonicated to ensure complete dissolution of byproducts, collected by centrifugation (8000 rpm for 5 min), and then washed five times with 20 mL of methanol. Upon drying at room temperature under vacuum, the bimetallic NPs with an Au to Cu mole ratio of 1:1 was obtained. By changing the stoichiometry of copper bromide and gold chloride, the NPs with different Au and Cu molar ratio can be obtained.

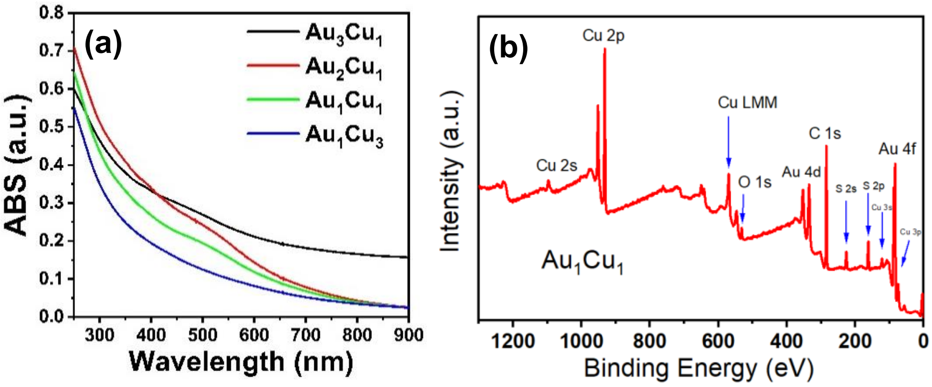


Fig. S7 (a)UV-vis absorption spectra of Au-Cu bimetallic NPs with different gold and copper molar ratio, (b) The XPS survey spectrum of Au_1Cu_1 bimetallic NPs.

S4 Synthesis of Au-Ag-Cu trimetallic nanoparticles by the Brust-Schiffrin method

We dissolved TOAB (1.5 g, 2.74 mmol) in 80 ml toluene and stirred until it had completely dissolved. Then, $AgNO_3$ (0.033 g, 0.195 mmol) in 5 mL of deionized water was added firstly and then NaBr (0.32 g, 3.12 mmol) solid was added. After continuous stirring, the pale-yellow AgBr precipitate gradually disappeared and the organic phase becomes clear. Then, $HAuCl_4·4H_2O$ (0.16 g 0.39 mmol) in 1 mL of water was added to the flask. The organic phase turned to deep reddish brown immediately, and continued to stir for 5 min, then $CuBr_2$ (0.044 g, 0.195 mmol) in 1 mL of water was added. After stirring for another 5 min, the water phase changes from blue to light-blue. Then, 1-hexanethiol (0.37 g, 3.12 mmol) was added to the solution after which the organic phase gradually became colorless and the aqueous phase became colorless. After stirring for 10 minutes, 20 mL of freshly prepared $NaBH_4$ (0.28 g, 7.4 mmol) aqueous solution was quickly poured into the flask and the organic phase quickly turned black. The organic phase was collected after 4 h of reaction and the organic solvent was removed using a rotary evaporator at a temperature below 50 °C. The remaining black muddy product was suspended in 30 mL of methanol, briefly sonicated to ensure complete dissolution of byproducts, collected by centrifugation (8000 rpm for 5 min), and then washed five times with 20 mL of methanol. Upon drying at room temperature under vacuum, the trimetallic nanoparticles with Au to Ag to Cu molar ratio of 2:1:1 were obtained. By changing the stoichiometry of silver nitrate, gold chloride and copper bromide, NPs with tunable Au, Ag and Cu molar ratio can be obtained.

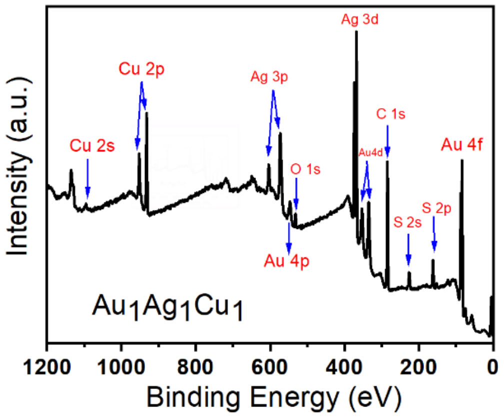


Figure S8 The XPS survey spectrum of $Au_1Ag_1Cu_1$ trimetallic NPs.

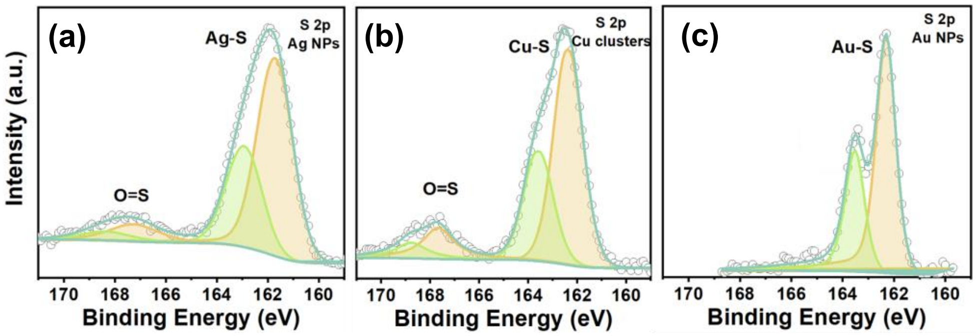
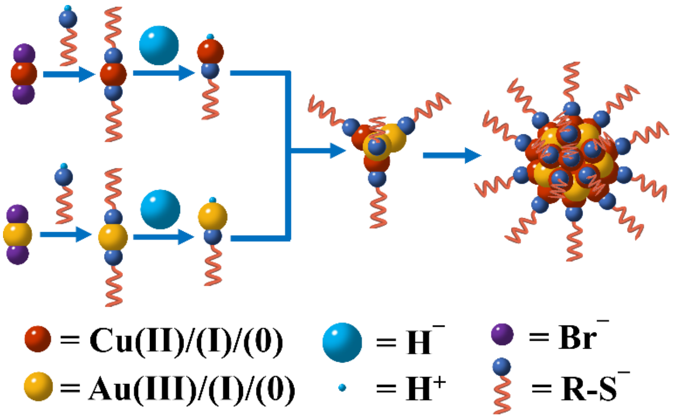


Fig. S9 The binding energy S 2p in XPS spectra of (a) Ag NPs, (b) Cu nanoclusters and Au NPs.



Scheme S1 Illustration of the proposed mechanism for synthesis of Au-Cu bimetallic NPs.