Facet-dependent Reduction Reaction of Diruthenium Metal String Complex by Face-to-Face Linked Gold Nanocrystals

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Supporting information: Synthesis methods, Absorption spectra, ECSERS spectra, and TEM and SEM images on SERS samples
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Synthesis methods of different shapes of Au nanocrystal.

**AuNS**

In brief, 0.5 mL of 0.029 M HAuCl$_4$(aq) was added to 49.5 mL water and heated at 70 °C. After added 0.1 g sodium citrate, the mixture was heated and stirred until the color changed to red.

**AuNR**

For *CTAB seed solution*, 86 μL 0.029 M HAuCl$_4$(aq) and 0.282 g CTAB were added into 7.75 mL water, subsequently, plugged into iced 600 μL 0.1 M NaBH$_4$(aq) under stirring and then placed 30 min. The growth step was carried out by adding 138 μL of 0.029 M HAuCl$_4$(aq), 15 μL of 0.01 M AgNO$_3$(aq) and 0.346 g CTAB in 10 mL water, followed by the addition of 60 μL of 0.1 M ascorbic acid aqueous solution and shaked until clear. Consequently, 40 μL of *CTAB seed solution* was added to the solution and aged overnight.

**AuRD, AuNC and AuOh**

For *CTAC seed solution*, 86 μL 0.029 M HAuCl$_4$(aq) and 0.32 g CTAC were added into 10 mL water, subsequently, plugged into iced 450 μL 0.02 M NaBH$_4$(aq) under stirring and then placed 30 min. Then, two growth steps were performed. The *growth solution* was carried out by adding 86 μL of 0.029 M HAuCl$_4$(aq) and 0.32 g CTAC in 10 mL water, followed by addition of 10 μL of 0.01 M NaBr(aq) and 79 μL of 0.04 M ascorbic acid aqueous solution and shaked until clear. Consequently, 45 μL of *CTAC seed solution* was added to the *growth solution*, and then transferred 45 μL of the mixture into additional *growth solution*. After aged overnight at constant 30 °C, the AuNC was synthesized with sizes ~50 nm. Varied nanocrystal shapes were obtained by varying portions of the ascorbic acid aqueous solution, *i.e.*, 127 and 170 μL of 0.04 M ascorbic acid aqueous solution for AuRD and AuOh, respectively. Besides, 5 μL of 0.01 M KI was added instead of NaBr for AuOh.

![Figure S1](image_url)

Figure S1. SEM (top) and TEM (bottom) images of Au nanocrystals. (a) AuNS, (b) AuNC, (c) AuOh, (d) AuRD, and (e) AuNR. The scale bars are 100 and 20 nm for SEM and TEM, respectively.
Figure S2. Absorption spectrum of $\text{[Ru}_2\text{(OAc)}_3(\text{bpnp})\text{]}^{\text{+}}\text{[PF}_6\text{]}^{-}$ which bears a [Ru$_2$]$^{4+}$ core in solvent dichloromethane. L denotes bpnp in this plot.
Figure S3. Raman spectra of Ru$_2$Cu(dpa)$_4$Cl$_2$ (top) and [Ru$_2$Cu(dpa)$_4$Cl$_2$]PF$_6$ (bottom) in crystal form by 632.8 nm excitation.
Figure S4. ECSERS spectra of Ru$_2$Cu(dpa)$_4$Cl$_2$ at -0.4–+1.2 V in 0.1 M TBAP/DCM by 785 nm excitation.
Figure S5. ECSERS spectra of Ru$_2$Ni(dpa)$_4$Cl$_2$ at no applied volt, +0.7, +1.1, and +1.2 V in 0.1 M TBAP/DCM by 632.8 (left) and 785 (right) nm excitation.