Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information of

Reaction Stoichiometry Directs the Architecture of Trimetallic Nanostructures Produced *via* Galvanic Replacement

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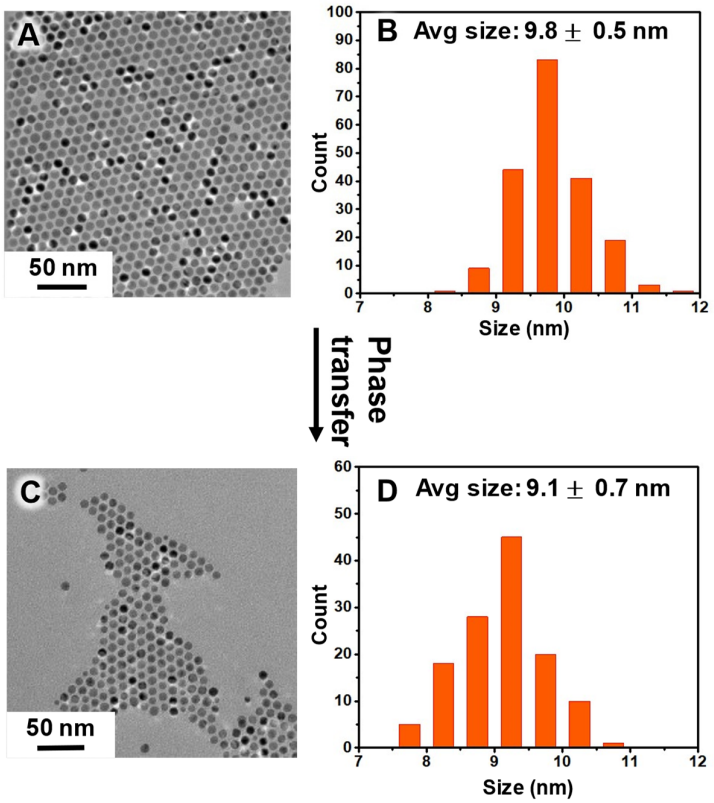

Figure S1. TEM images and size histogram of i-PdCu seeds before phase transfer (A-B) and after phase transfer (C-D).

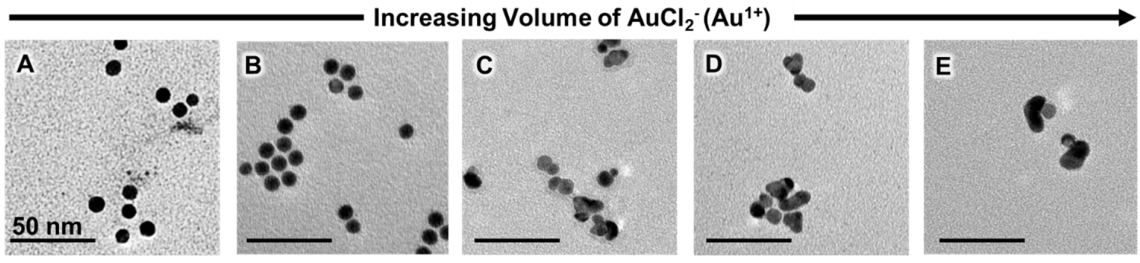

Figure S2. TEM images showing 5 different stages involved in the galvanic replacement reaction, in which i-PdCu nanoparticles are titrated with A) 0.5, B) 1.5, C) 4.5, D) 9, and E) 25 mL of 0.1 mM $AuCl_2^-$. All scale bars present 50 nm. Figure 2B, C, and D correspond to the same sample in Figures 1D, E, and F respectively.

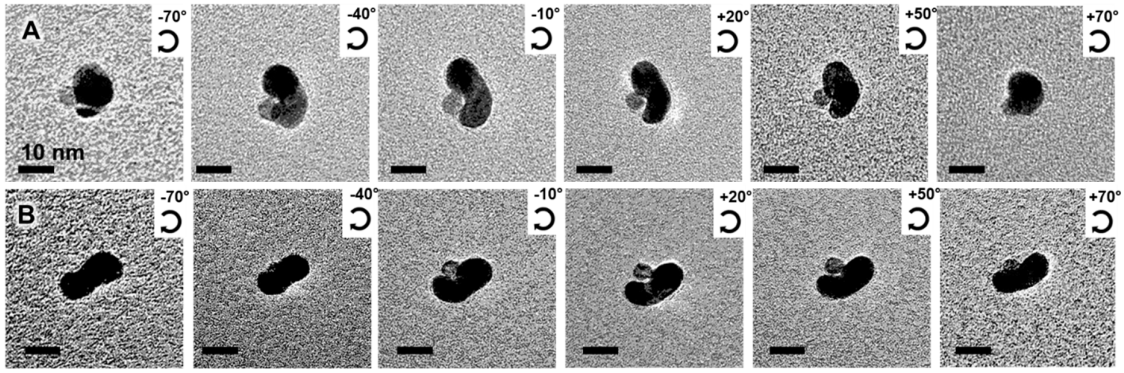

Figure S3. Electron tomography showing TEM images of the same i-PdCu-Au heterostructure NPs rotated along the (A) A-axis and (B) B-axis.

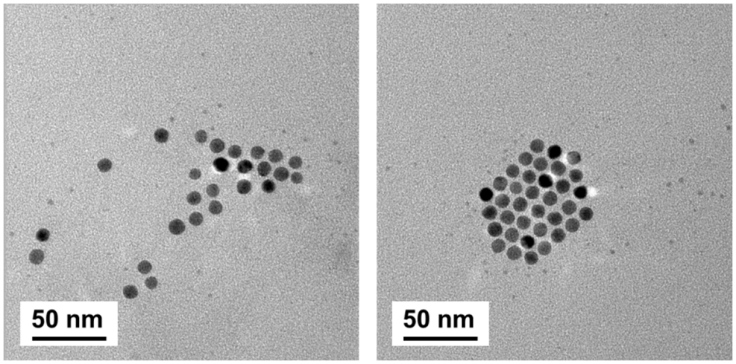

Figure S4. Low magnification TEM images of galvanic replacement products obtained from adding 0.5 mL 0.1 mM $AuCl_4^-$ to i-PdCu template.

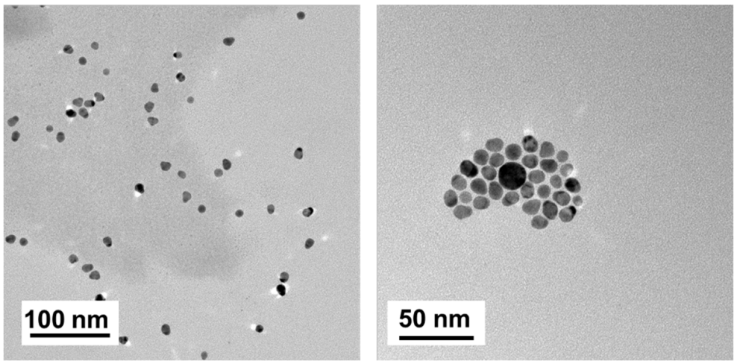

Figure S5. Low magnification TEM images of galvanic replacement products obtained from adding 1.5 mL 0.1 mM $AuCl_4^-$ to i-PdCu template.

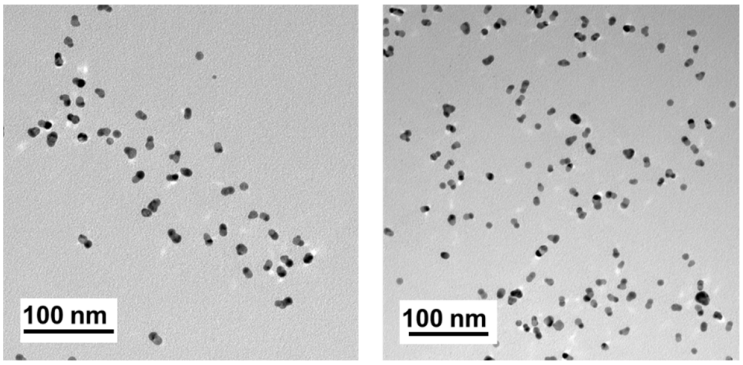

Figure S6. Low magnification TEM images of galvanic replacement products obtained from adding 3 mL 0.1 mM $AuCl_4^-$ to i-PdCu template.

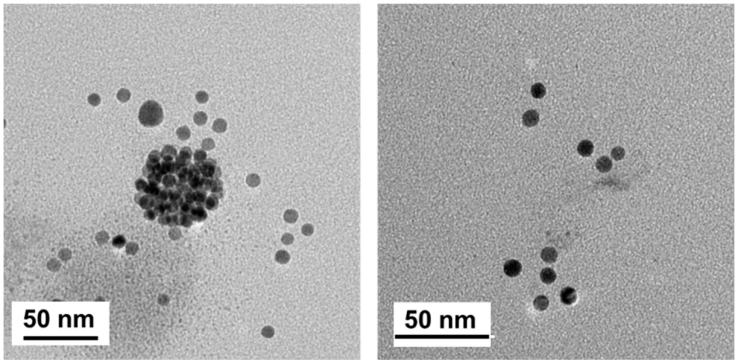

Figure S7. Low magnification TEM images of galvanic replacement products obtained from adding 0.5 mL 0.1 mM $AuCl_2^-$ to i-PdCu template.

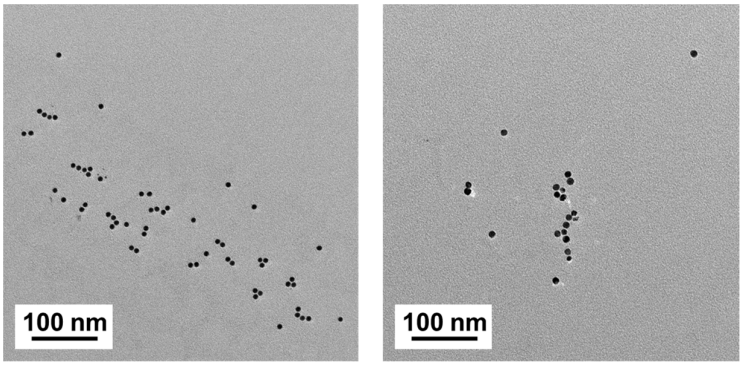

Figure S8. Low magnification TEM images of galvanic replacement products obtained from adding 1.5 mL 0.1 mM $AuCl_2^-$ to i-PdCu template.

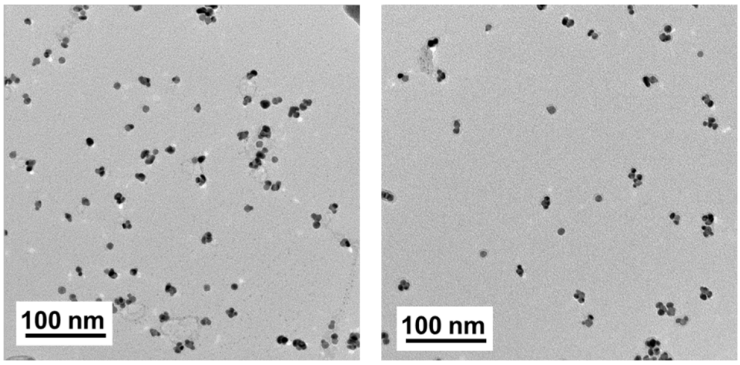

Figure S9. Low magnification TEM images of galvanic replacement products obtained from adding 4.5 mL 0.1 mM $AuCl_2^-$ to i-PdCu template.

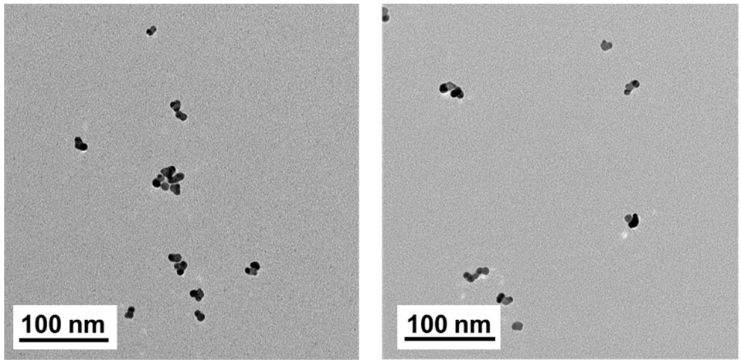

Figure S10. Low magnification TEM images of galvanic replacement products obtained from adding 9 mL 0.1 mM $AuCl_2^-$ to i-PdCu template.

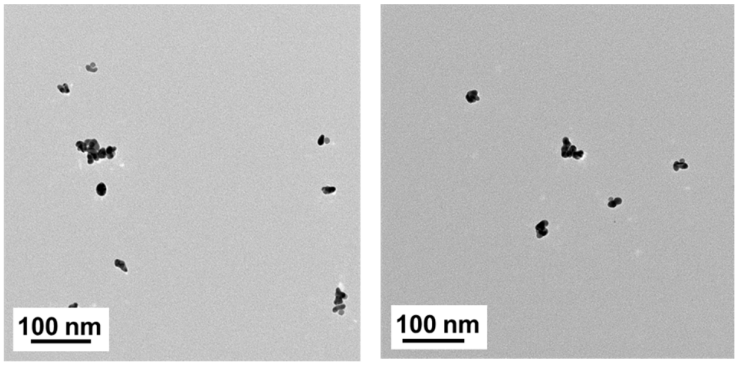

Figure S11. Low magnification TEM images of galvanic replacement products obtained from adding 25 mL 0.1 mM $AuCl_2^-$ to i-PdCu template.

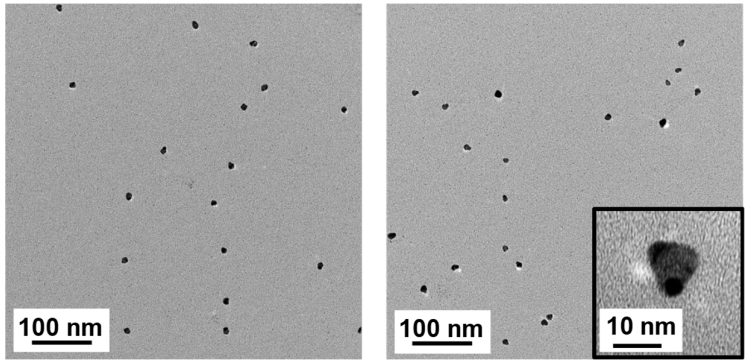

Figure S12. Low magnification TEM images of galvanic replacement products obtained from adding 1.5 mL 0.3 mM $AuCl_2^-$ to i-PdCu template.

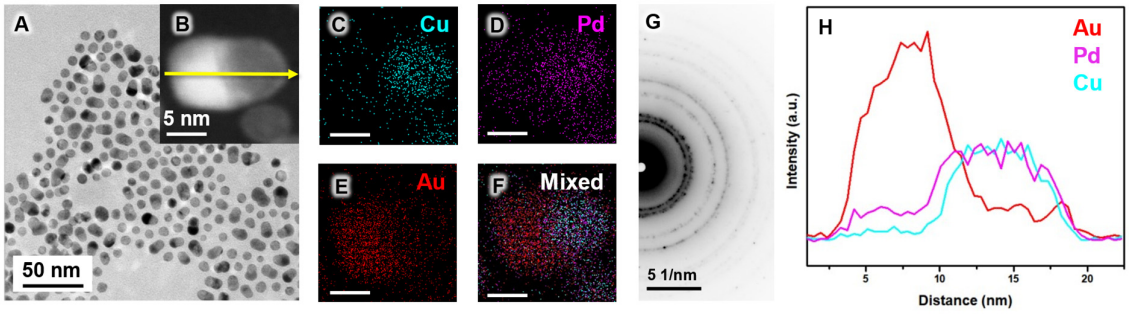

Figure S13. A) Low magnification TEM image, B-F) STEM image and elemental mapping, G) coherent nano-area ED and H) line scan according to the yellow arrow of galvanic replacement product obtained from adding 3 mL 0.1 mM $AuCl_4^-$ in NaCl saturated solution to i-PdCu template. Cu: Cyan, Pd: Magenta, Au: Red.

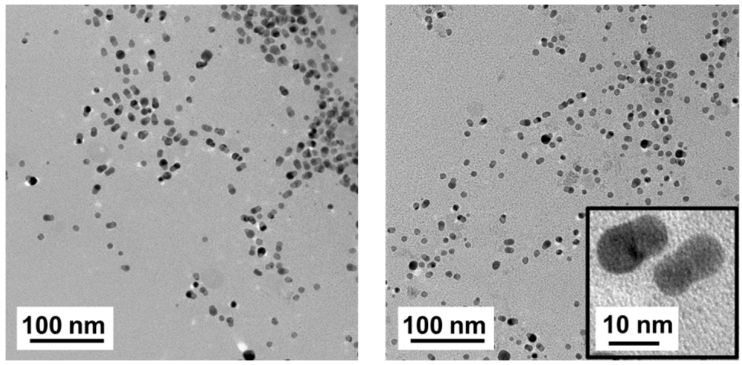

Figure S14. Low magnification TEM images of galvanic replacement products obtained from adding 4 mL 0.1 mM $AuCl_4^-$ of pH 7.5 to i-PdCu template.

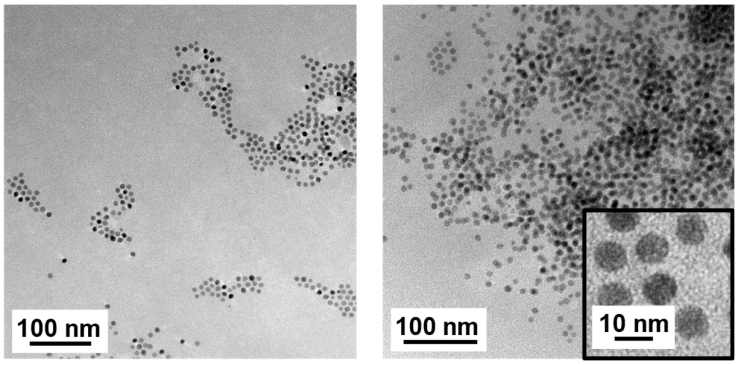

Figure S15. Low magnification TEM images of galvanic replacement products obtained from adding 4 mL 0.1 mM $AuCl_4^-$ of pH 12.5 to i-PdCu template.

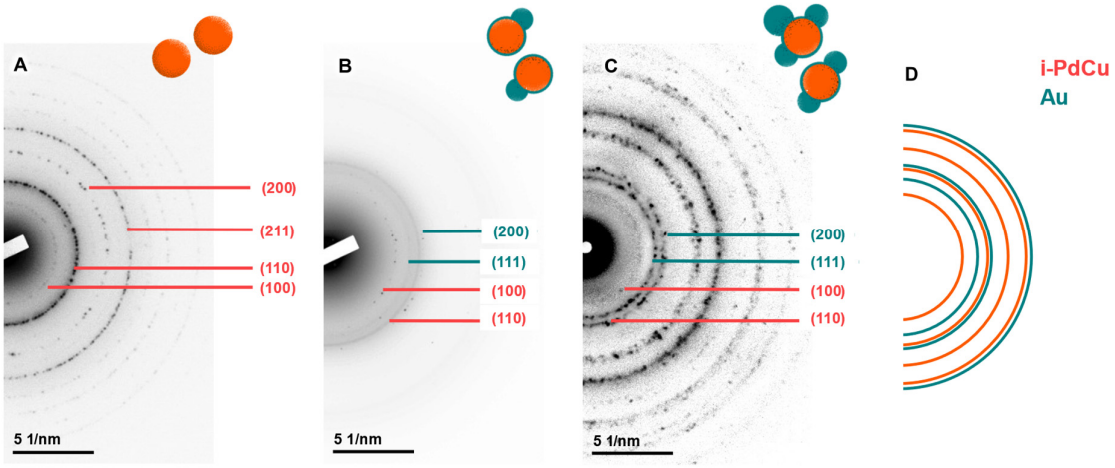

Figure S16. Selected area ED patterns for the A) i-PdCu, B) i-PdCu-Au heterostructures with $AuCl_2^-$, coherent nano-area ED pattern of C) i-PdCu-Au heterostructures with $AuCl_4^-$, D) i-PdCu-Au heterostructures simulated diffraction pattern shows distinct spots or rings for each of the components. i-PdCu: Orange, Au: Teal.

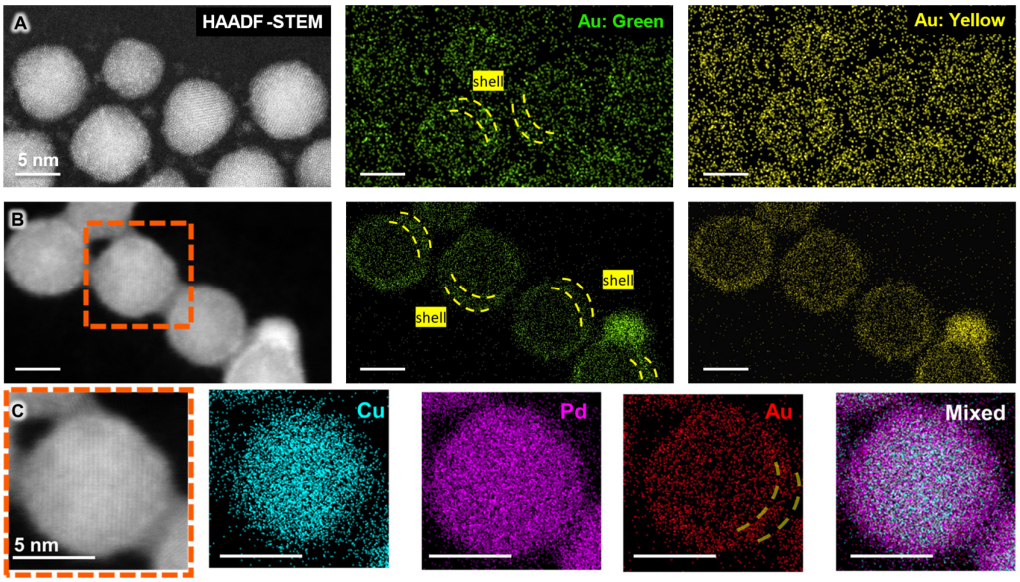

Figure S17. HAADF-STEM images and EDS maps of Au signal in green and yellow coloration showing of galvanic replacement products, core@shell i-PdCu@Au nanoparticles, when titrated with A) 1.5 mL of 0.1 mM $AuCl_2^-$ and B) 4.5 mL of 0.1 mM $AuCl_2^-$. C) Full elemental mapping of the orange dash highlighted NP in part B, where Cu: Cyan, Pd: Magenta, and Au: Red. The yellow dashed lines guide the shell location of the 2D mapping of a 3D NP. All scale bars are 5 nm.

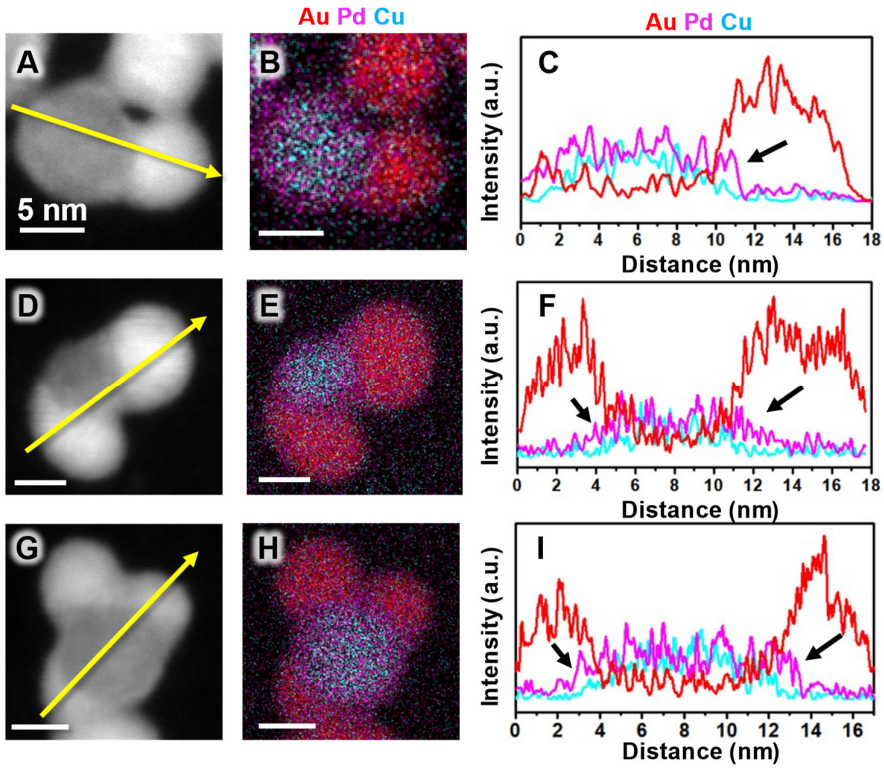

Figure S18. HAADF-STEM images, EDS maps, and line scan along the yellow line of galvanic replacement products showing i-PdCu-Au heterostructure nanoparticles (A-C) one domain, (D-F) two domains, (G-I) three domains when titrated with 4.5 mL of $AuCl_2^-$. Intersection areas are rich in Pd which are marked with arrows. Cu: Cyan, Pd: Magenta, Au: Red.

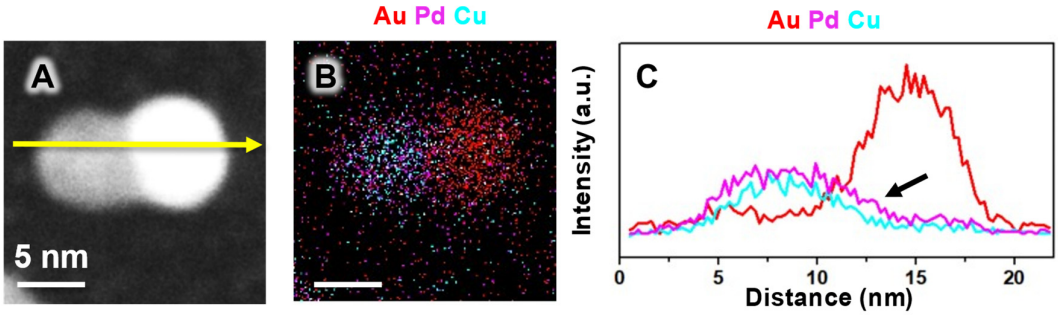

Figure S19. HAADF-STEM images, EDS maps, and line scan along the yellow line of galvanic replacement products showing i-PdCu-Au dimer nanoparticles when titrated with 3 mL of $AuCl_4^-$. Intersection areas are rich in Pd which are marked with arrows. Cu: Cyan, Pd: Magenta, Au: Red.

No.	Titrant type	Titrant concentration	Titrant volume	Rate of addition	Duration of reaction	Figures in SI	Figures in main text
1	$AuCl_4^-$	0.1 mM	0.5 mL	0.75 mL/min	10 min	Figure S4	Figure 2B
2	$AuCl_4^-$	0.1 mM	1.5 mL	0.75 mL/min	10 min	Figure S5	Figure 2C
3	$AuCl_4^-$	0.1 mM	3.0 mL	0.75 mL/min	10 min	Figure S6	Figure 2D
4	$AuCl_2^-$	0.1 mM	0.5 mL	0.75 mL/min	10 min	Figure S7	Figure 2E
5	$AuCl_2^-$	0.1 mM	1.5 mL	0.75 mL/min	10 min	Figure S8	Figure 2F
6	$AuCl_2^-$	0.1 mM	4.5 mL	0.75 mL/min	10 min	Figure S9	Figure 2G
7	$AuCl_2^-$	0.1 mM	9.0 mL	0.75 mL/min	10 min	Figure S10	Figure 2H
8	$AuCl_2^-$	0.1 mM	25 mL	0.75 mL/min	10 min	Figure S11	Figure 2I

Table S1. Summary of the parameters for each GR reaction including the titrant type, concentration, volume, rate of titrant addition using a syringe pump, duration of reaction, and corresponding figures which are presented in the main text and SI.

$AuCl_2^-$ volume added	Au (at%)	$AuCl_4^-$ volume added	Au (at%)
0.5	1.7	-	-
1.5	9.4	0.5	1.7
4.5	24.8	1.5	10.9
9.0	65.1	3.0	35.7
25.0	72.7	-	-

Table S2. The SEM-EDS percentages of gold, by atom, in the i-PdCu-Au heterostructures were obtained by titrating i-PdCu with different amounts of 0.1 mM $AuCl_2^-$ and $AuCl_4^-$.