

Electronic Supplementary Information

Synthesis of Core-Shell Au-Pt Nanodendrites with High Catalytic Performance *via* Overgrowth of Platinum on *in situ* Gold Nanoparticles

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Figure S1. HRTEM images of Pt nanobranches on CS Au-Pt₅ NDs with defects (such as atomic steps, kinks, and corner atoms). The concentrations of K₂PtCl₄, HAuCl₄, citrate and AA are 3.6, 0.70, 3.0 and 29.4 mM, respectively. The molar ratios of Pt-to-Au and AA-to-Pt are 5.0 and 8.0, respectively.

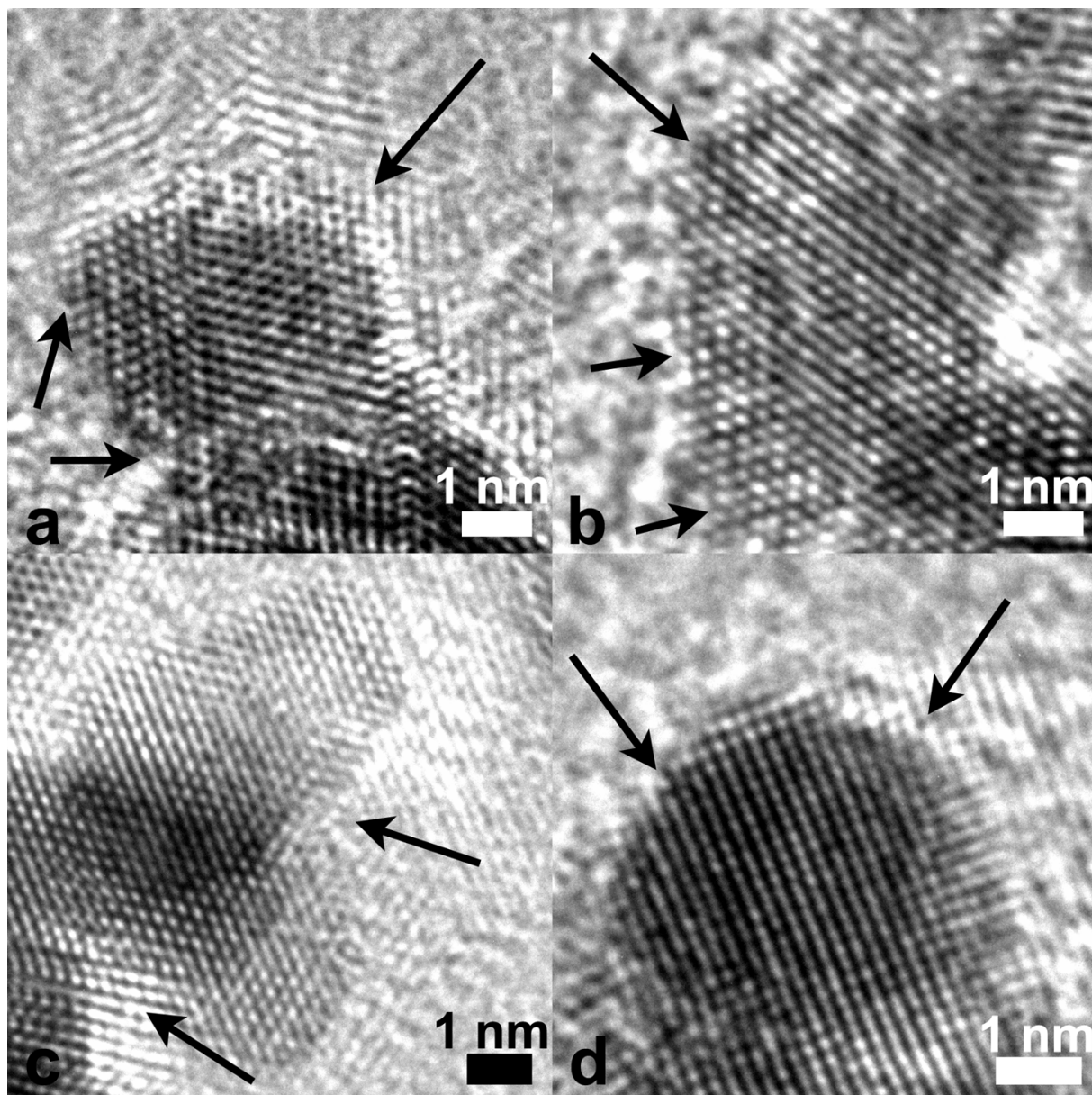


Figure S2. Selected area electron diffraction (SAED) pattern of the Au-Pt₅ NDs obtained. The concentrations of K₂PtCl₄, HAuCl₄, citrate and AA are 3.6, 0.70, 3.0 and 29.4 mM, respectively. The molar ratios of Pt-to-Au and AA-to-Pt are 5.0 and 8.0, respectively.

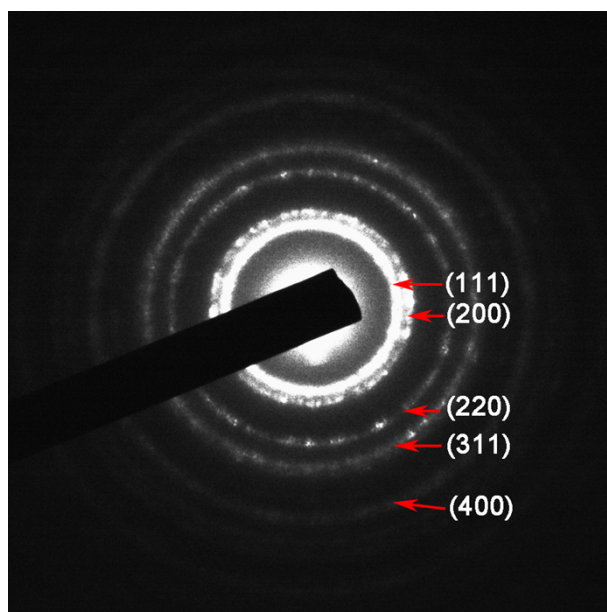


Figure S3. HAADF-STEM-EDS mapping images of the Au-Pt₅ NDs obtained. The concentrations of K₂PtCl₄, HAuCl₄, citrate and AA are 3.6, 0.70, 3.0 and 29.4 mM, respectively. The molar ratios of Pt-to-Au and AA-to-Pt are 5.0 and 8.0, respectively.

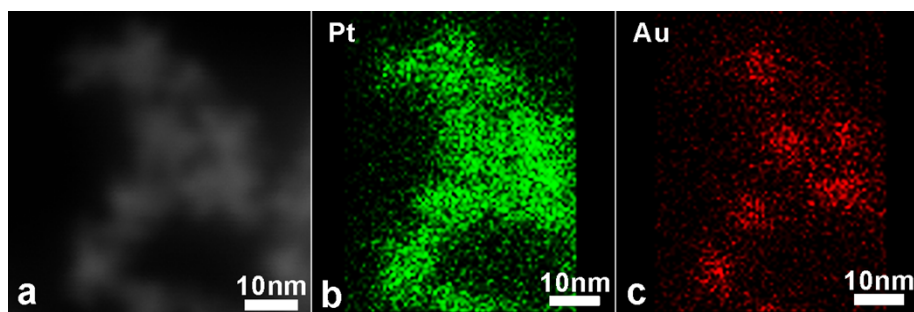


Figure S4. TEM images of other Au-Pt NDs obtained with incubation time of 9 min (a) and 18 min (b). The concentrations of K_2PtCl_4 , HAuCl_4 , citrate and AA are 3.6, 0.70, 3.0 and 29.4 mM, respectively. The molar ratios of Pt-to-Au and AA-to-Pt are 5.0 and 8.0, respectively.

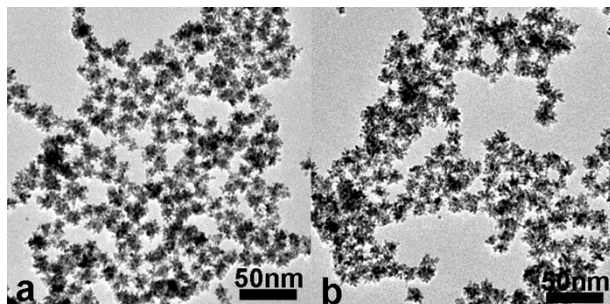


Figure S5. TEM image of nanowire-like Au crystals extracted from the citrate-HAuCl₄-K₂PtCl₆ solution with incubation time of 11 min. The final concentrations of K₂PtCl₆, HAuCl₄ and citrate are 4.2, 0.83 and 3.4 mM, respectively. The Pt-to-Au molar ratio is 5.0.

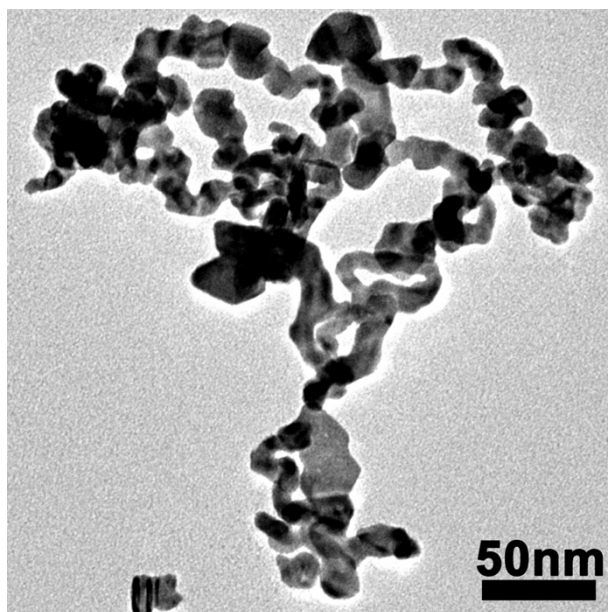


Figure S6. TEM image of the hyperbranched Pt particles prepared according to the literature. The concentrations of K_2PtCl_4 and AA are 12.5 mM and 50.0 mM, respectively.

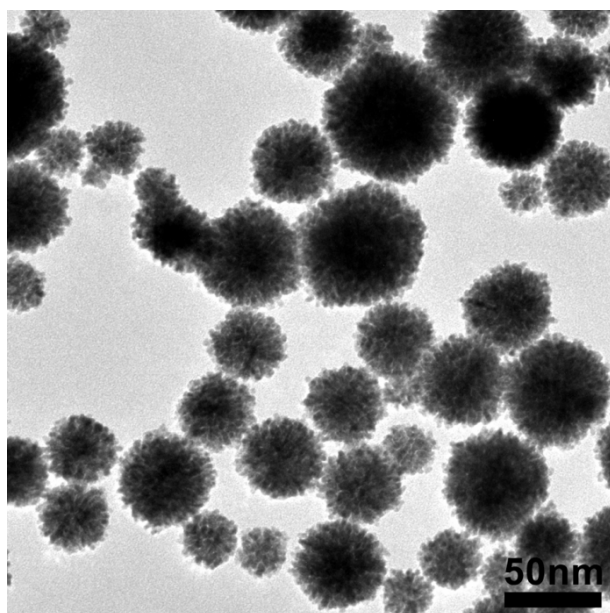


Figure S7. CV curves of GCEs modified by commercial Pt black (a, black curve), hyperbranched Pt nanoparticles (b, red curve), and Au-Pt₅ NDs (c, blue curve) measured in 0.50 M H₂SO₄ solution in the presence of 1.0 M methanol. The scan rate is 20 mV s⁻¹. The currents are normalized by the ECSA values.

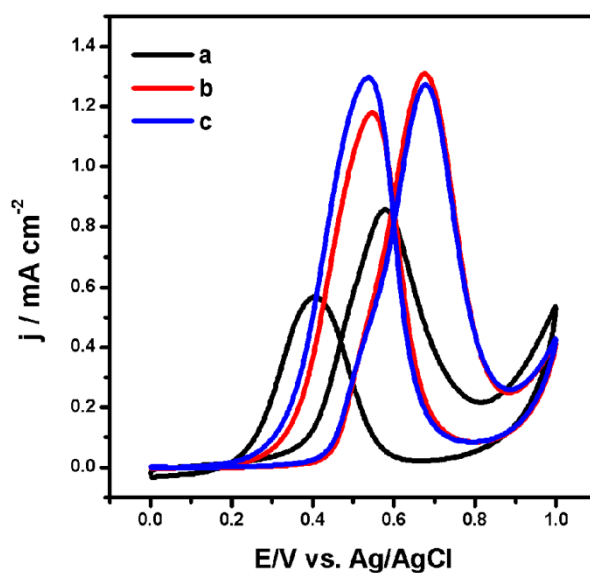


Figure S8. Pt 4f XPS spectra of spherical hyperbranched Pt particles (a) and CS Au-Pt₅ NDs (b).

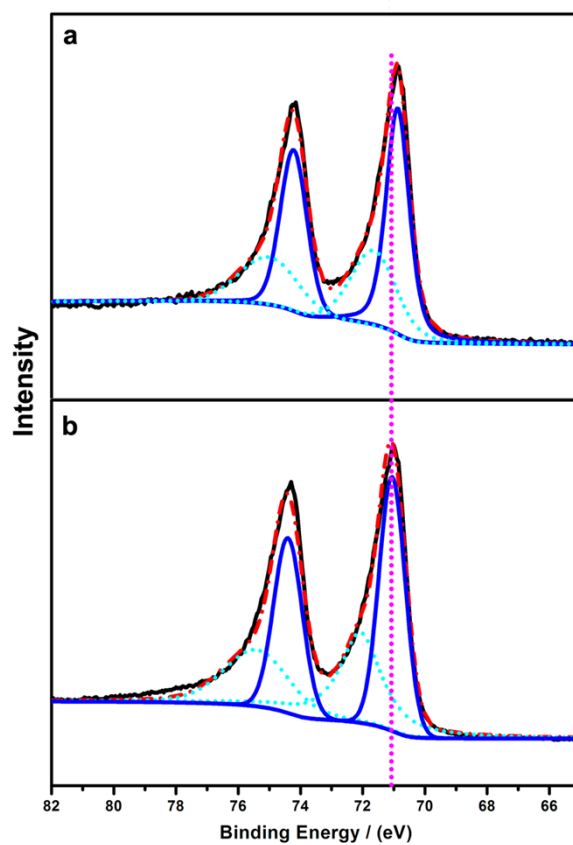


Figure S9. (A) Cyclic voltammograms of GCE modified by commercial Pt black (a, black curve), hyperbranched Pt nanoparticles (b, red curve), and Au-Pt₅ NPs (c, blue curve) measured in 0.10 M H₂SO₄ solution after immersion in CO saturated 0.1 M H₂SO₄ for 10 min at a potential of -0.2 V. (B) Cyclic voltammograms of GCE modified by Au-Pt_{2.5} particles (a, black curve), Au-Pt₄ NPs (b, red curve), Au-Pt₅ NPs (c, blue curve), and Au-Pt₆ NPs (d, magenta curve) measured in 0.10 M H₂SO₄ solution after immersion in CO saturated 0.1 M H₂SO₄ for 10 min at a potential of -0.2 V. The scan rate is 50 mV s⁻¹. The currents are normalized by the Pt mass loaded.

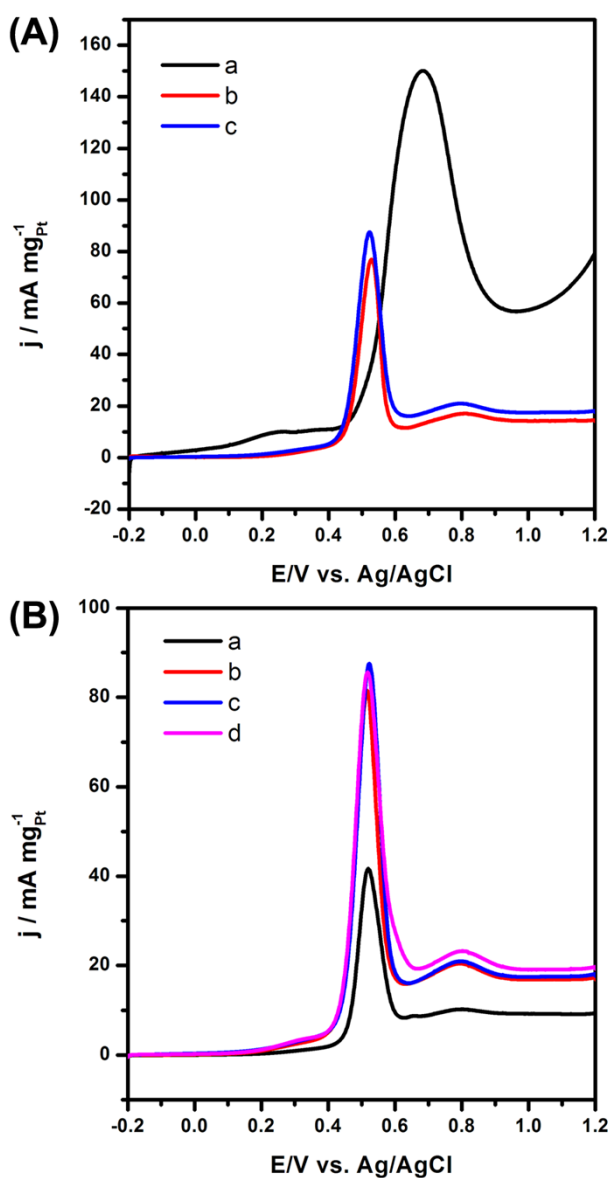


Figure S10. Potential cycling stability of MOR catalyzed by Pt black (a) and CS Au-Pt₅ NDs (b), measured in 0.5 M H₂SO₄ in presence of 1.0 M methanol solution. The scan rate is 50 mV s⁻¹.

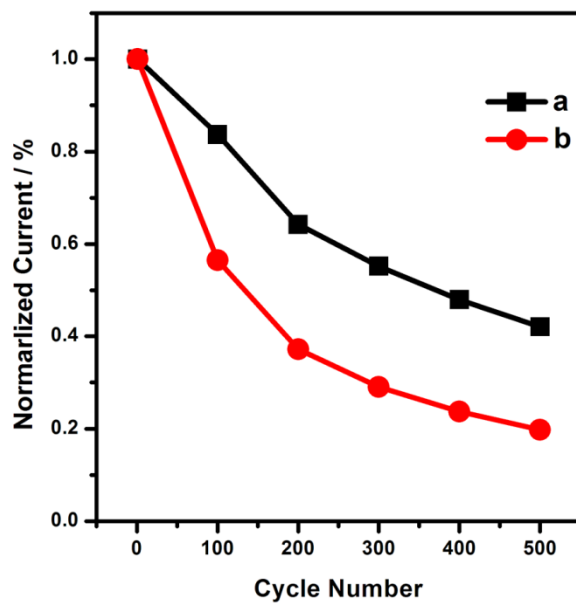


Figure S11. TEM image of CS Au-Pt₅ NDs after cycling stability test.

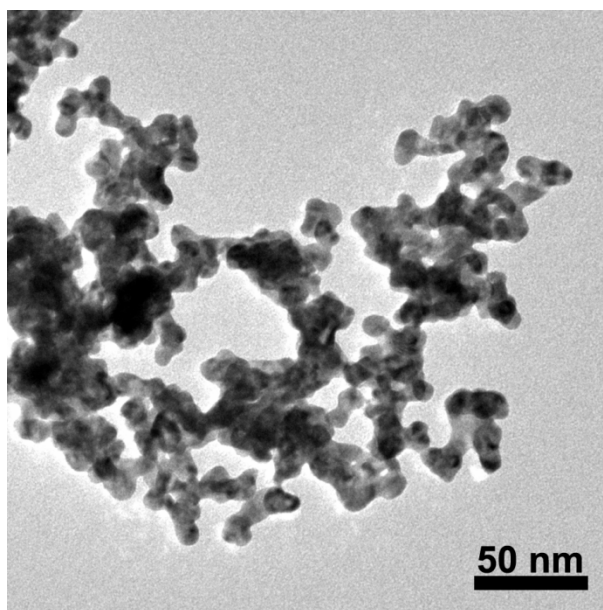


Table S1. Summary of the redox potential values of half-reaction of $\text{AuCl}_4^-/\text{Au}^0$ and $\text{PtCl}_6^{2-}/\text{PtCl}_4^{2-}$.

Half-reaction	Potential values (V)
$\text{AuCl}_4^- + 3\text{e} \leftrightarrow \text{Au}^0 + 4\text{Cl}^-$	1.002
$\text{PtCl}_6^{2-} + 2\text{e} \leftrightarrow \text{PtCl}_4^{2-} + 2\text{Cl}^-$	0.68

Table S2. Summary of ECSAs, current densities normalized by mass and current densities normalized by ECSA of GCE modified by Au-Pt_m products with different Pt-to-Au molar ratios. The AA-to-Pt molar ratio is 8.0.

Pt-to-Au molar ratio	ECSA [m² g⁻¹]	Mass activity [A mg⁻¹]	Specific activity [mA cm⁻²]
1	22.2	0.13	0.57
2.5	25.3	0.29	1.13
4	30.3	0.35	1.14
5	35.2	0.45	1.27
6	34.3	0.40	1.16

Table S3. Summary of the lengths and widths of the branches on Au-Pt₅ nanodendrites prepared under different AA-to-Pt molar ratios. The concentrations of K₂PtCl₄, HAuCl₄, citrate and AA are 3.6, 0.70, 3.0 and 29.4 mM, respectively. The Pt-to-Au molar ratio is 5.0.

AA-to-Pt molar ratio	2/1	4/1	8/1
Length (nm)	3.7	3.8	4.2
Width (nm)	2.8	2.6	2.6