

Supporting information

Low-Temperature Seeding-Assisted Synthesis of Monodispersed Hyperbranched PtRu Nanoparticles and Their Electrocatalytic Activity in Methanol Oxidation

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1. Experimental detail

1.1 Preparation of hyperbranched Pt NPs

Potassium tetrachloroplatinate (K_2PtCl_4 , Aldrich, >99.9%) was dissolved in ultraclean de-ionized (DI) water (Aqua, 18.2 M Ω) to prepare K_2PtCl_4 stock solution of 10 mM and aged for at least 48 h before being used. Ruthenium(III) chloride hydrate ($\text{RuCl}_3 \cdot x\text{H}_2\text{O}$, Aldrich, 99.98%) was dissolved in water to prepare RuCl_3 stock solution of different concentrations such as 10, 20 mM. Peptide molecules (with sequence Ser-Ser-Phe-Pro-Gln-Pro-Asn, termed as S7) were used as capping agent for the synthesis. S7 stock solution was prepared by dissolving 1 mg of S7 peptide in 1 mL of water. Reaction solution were prepared by mixing 200 μL of K_2PtCl_4 stock solution, 100 μL of peptide stock solution, and 2.8 mL of DI water and kept stirred for 5 min before reaction. Fresh 40 mM sodium borohydride (NaBH_4) solution was prepared immediately before reaction by dissolving 15 mg NaBH_4 (Aldrich, 99.99%) in 10 mL DI water.

Reaction was carried out by injecting 100 μL NaBH_4 solution in a single shot into the reaction vessel containing K_2PtCl_4 and S7 peptide. After 30 s, 800 μL RuCl_3 stock solution was injected in another shot into the reaction solution. The reaction solution was centrifuged after 1 h of reaction and the precipitated NPs were collected and re-dispersed in 1 mL DI water.

TEM samples were prepared by floating the carbon side of the copper grid on a drop of NP solution for 5 min and then on a drop of DI water for another 3 min. The grid was dried in air at room temperature. TEM images were obtained on FEI CM 120 operated at 120 kV. HRTEM images, HAADF images, and EDS were captured on FEI TITAN STEM operated at 300 kV.

UV-Vis spectra were obtained from DU[®]800 Spectrophotometer. XRD pattern were obtained from panalytical X'pert pro diffractometer. Weight concentration of the NP

solution was determined by inductively coupled plasma optical emission spectrometry (ICP-OES).

1.2 Electrochemical measurement

NP solutions were diluted to 0.5 mg/mL based on the concentrations measured by ICP-OES. Working electrodes were prepared by pipetting 8 μ L of NP solution onto a glassy carbon electrode with a diameter of 3mm and dried at 60 $^{\circ}$ C. A Nafion solution of 0.05% was then pipetted to the electrode and dried to cover the NP layer. Commercially available PtRu black (1:1 in atomic ratio, Alfa Aesar) and Pt black (Alfa Aesar) were used as comparison.

Electrochemical surface areas were determined by UPD Cu stripping approach. Ag/AgCl electrode and Pt wire were used as reference electrode and counter electrode, respectively. All potentials mentioned are recorded vs. Ag/AgCl reference electrode. In 0.1 M H_2SO_4 electrolyte, the electrode was kept at 0.8V for 120 s, and then 0.1 V for 150 s, and followed with linear scan from 0.1 to 0.8 V at the rate of 10 mV/s. The same electrochemical treatment was done in the electrolyte with 0.1 M H_2SO_4 and 0.005 M CuSO_4 . The charge induced by Cu desorption was calculated by subtracting the currents of the two curves and integrating the current with respect to time. Area was calculated by dividing the charge by monolayer stripping charge of Cu, 420 $\mu\text{C}/\text{cm}^2$.

Cyclic voltammograms (CVs) were recorded in 0.1 M H_2SO_4 electrolyte with 0.5 M methanol at a scan rate of 100 mV/s between -0.2 and 1 V. The obtained CV curves were normalized by the area determined by Cu UPD approach.

2. HRTEM image of PtRu black.

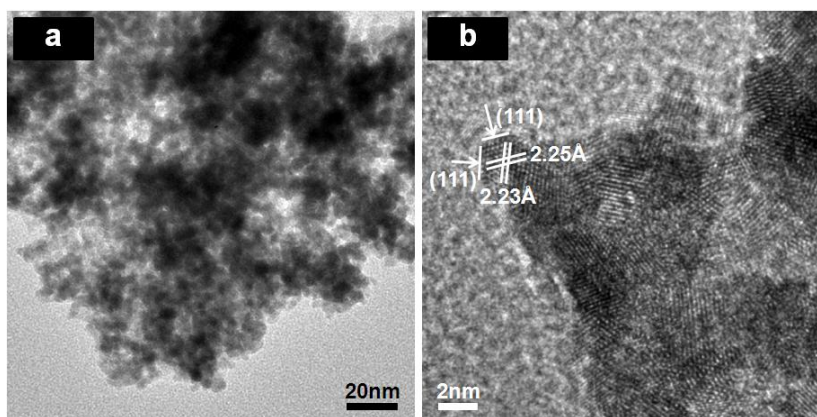


Figure S1. (a) Low magnification TEM image and, (b) HRTEM image of PtRu black, respectively.

3. Capture of Pt seeds.

40 mM NaBH₄ (100 µL) solution was injected into solution containing 1 mM K₂PtCl₄ and 25 µg/mL S7 peptide molecule. S7 peptide was used as capping agent, as reported in previous work published from our group.^[1] Pt seeds were captured by taking reaction solution 30 s after the NaBH₄ injection and casting onto the TEM grids followed by wash with DI water.

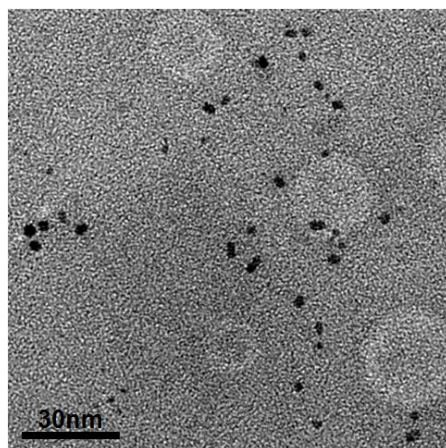


Figure S2. TEM images of the Pt NPs captured at 30 s and after injecting 1 mM NaBH₄ into the mixed solution of 0.5 mM K₂PtCl₄ and 25 µg/mL S7.

4. PtRu and Ru NPs synthesized without Pt seed NCs.

As comparisons with the synthesis of PtRu HBNPs, PtRu and Ru NPs were synthesized without the Pt seed NCs. For the PtRu NPs shown in Fig. S3(a), an aqueous solution of 3.1 mL with 25 µg/mL S7 (final concentration) was prepared and stirred for 5 min. Then, 400 µL of 5 mM K₂PtCl₄, and 400 µL of 5 mM RuCl₃ solutions were injected simultaneously 30 s after the injection of 100 µL of 40 mM NaBH₄. For the Ru NPs in Fig. S3(b), a solution of 3.5 mL with 25 µg/mL S7 was prepared and stirred for 5 min. Then, only 400 µL of 5 mM RuCl₃ solution was injected 30 s following the injection of 100 µL of 40 mM NaBH₄.

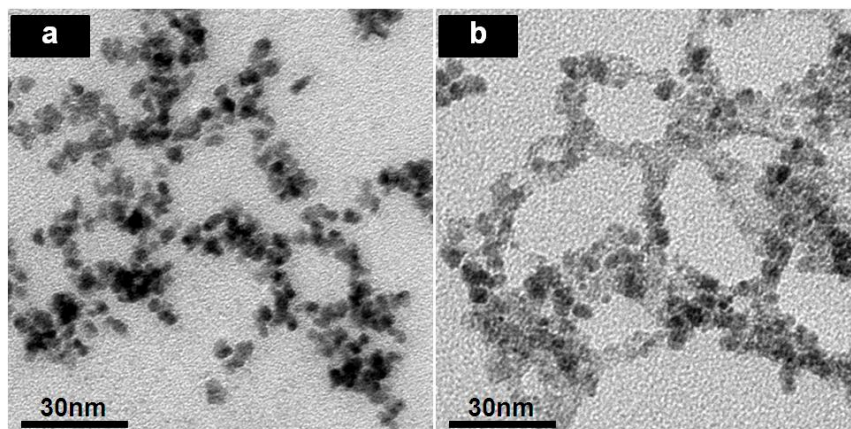


Figure S3. (a) PtRu NPs synthesized by injecting 0.5 mM K_2PtCl_4 and 0.5 mM RuCl_3 into solution with 1 mM NaBH_4 and 25 $\mu\text{g/mL}$ S7. (b) Ru NPs synthesized by injecting 0.5 mM RuCl_3 into solution with 1 mM NaBH_4 and 25 $\mu\text{g/mL}$ S7.

5. Pt NPs grown without adding RuCl_3 .

40 mM NaBH_4 (100 μL) solution was injected into solution containing 1 mM K_2PtCl_4 and 25 $\mu\text{g/mL}$ S7 peptide molecule. Pt NPs were captured by taking reaction solution 1 h after the NaBH_4 injection and casting onto the TEM grids followed by washing with DI water.

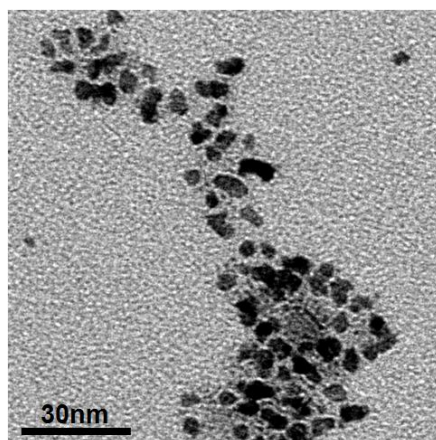


Figure S4. TEM images of the Pt NPs 1 h after injecting 1 mM NaBH_4 into the mixed solution of 0.5 mM K_2PtCl_4 and 25 $\mu\text{g/mL}$ S7.

6. Capture the existence of Ru^{2+} .

Images were taken with video mode of Canon S5 camera. 100 μL of fresh NaBH_4 solution was firstly injected into reaction solution containing 1 mM K_2PtCl_4 and 25 $\mu\text{g/mL}$ S7 peptide. And then 800 μL of 5 mM RuCl_3 solution was injected into the solution. Figure S5(a) is the snapshot taken from video, which is at 0.1 s from the start of RuCl_3 injection. All images show original color without any color processing.

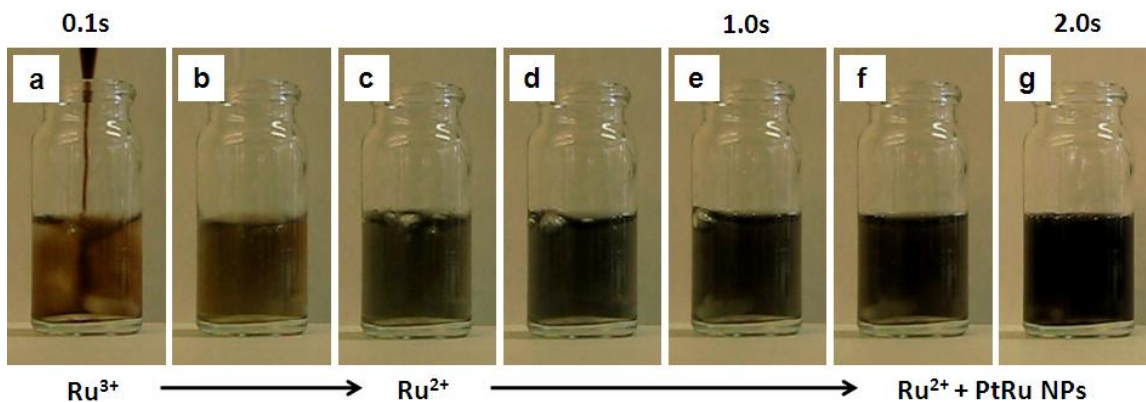


Figure S5. (a-g) Snapshots of video recorded showing the color change of reaction solution in 2 s after the RuCl_3 injection.

7. Electrochemical surface areas of Different catalyst

Table S1. Electrochemical surface areas (measured by Cu UPD method) of different catalysts used in this study.

Catalyst	ECSA (m^2/g)
Pt black	18.2
PtRu black	36.6
Pt_3Ru HBNP	57.9
Pt_4Ru HBNP	65.4
IR $\text{Pt}_{1.2}\text{Ru}$	77.4
IR $\text{Pt}_{1.8}\text{Ru}$	75.0

8. Methanol oxidation by irregular (IR) PtRu nanoparticles

IR $\text{Pt}_{1.2}\text{Ru}$ nanoparticles were synthesized by adding 100 μL of 40 mM NaBH_4 solution into 3.9 mL mixed solution with 0.4mM K_2PtCl_4 , 0.6 mM RuCl_3 and 25 $\mu\text{g}/\text{mL}$ S7 peptide. Irregular $\text{Pt}_{1.8}\text{Ru}$ nanoparticles were synthesized by adding 100 μL of 40 mM NaBH_4 solution into 3.9 mL mixed solution with 0.6 mM K_2PtCl_4 , 0.4 mM RuCl_3 and 25 $\mu\text{g}/\text{mL}$ S7 peptide. TEM images of the IR PtRu NPs were shown in Fig. S6. The comparison of methanol oxidation performances of Pt_3Ru , Pt_4Ru HBNPs with IR $\text{Pt}_{1.2}\text{Ru}$, $\text{Pt}_{1.8}\text{Ru}$ NPs were shown in Fig. S7.

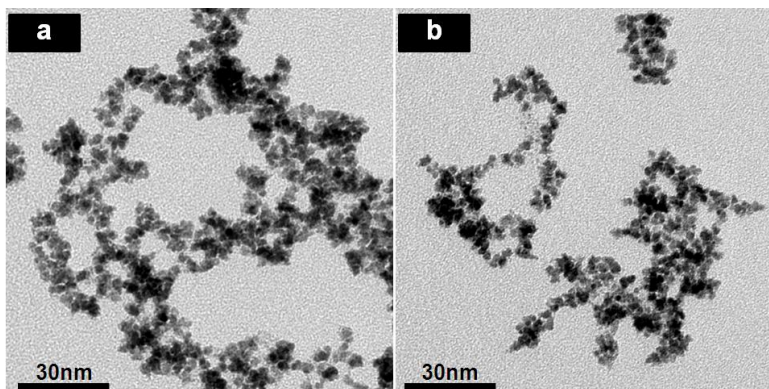


Figure S6. (a) and (b) are TEM images of IR $\text{Pt}_{1.2}\text{Ru}$ and $\text{Pt}_{1.8}\text{Ru}$ NPs.

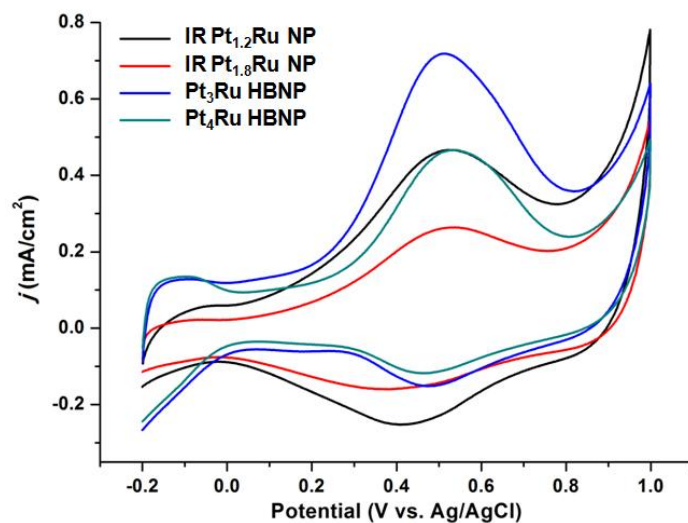


Figure S7. CV curves of Pt₃Ru and Pt₄Ru HBNPs, and IR Pt_{1.2}Ru and Pt_{1.8}Ru NPs.

References

- [1] C. Y. Chiu, Y. Li, L. Ruan, X. Ye, C. B. Murray, Y. Huang, *Nat. Chem.* **2011**, 3, 393-399.