

Highly Selective Synthesis of Catalytically Active Monodisperse Rhodium Nanocubes

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Experimental Section

1. Chemicals. Rhodium(III) chloride hydrate ($\text{RhCl}_3 \cdot x\text{H}_2\text{O}$; Sigma-Aldrich), rhodium(III) bromide hydrate ($\text{RhBr}_3 \cdot x\text{H}_2\text{O}$; Sigma-Aldrich) ammonium hexachloroplatinate(IV) ($(\text{NH}_4)_2\text{PtCl}_6$, 99.999%; Sigma-Aldrich), ammonium hexachloropalladate (IV) ($(\text{NH}_4)_2\text{PdCl}_6$, 99.99%; Sigma-Aldrich), poly(vinylpyrrolidone) (PVP, $M_w = 24,000$; Sigma-Aldrich), trimethyl(tetradecyl)ammonium bromide ($(\text{C}_{14}\text{H}_{29})\text{N}^+(\text{CH}_3)_3\text{Br}^-$, 99%; Sigma-Aldrich), ethylene glycol (>98%; EMD), and the solvents (analytical grade) including acetone, ethanol, hexanes and chloroform were used without further purification.

2. Synthesis of Rh Nanocubes. 0.2 mmol rhodium(III) chloride hydrate, 1 mmol trimethyl(tetradecyl)ammonium bromide, and 4 mmol poly(vinylpyrrolidone) (in terms of the repeating unit) were added to 20 ml ethylene glycol in a 50 ml three-necked flask at room temperature. The stock solution was heated to 80 °C in a Glas-Col electromantle (60 W; 50 ml) with a Cole-Parmer temperature controller (Digi-sense®), and was evacuated at this temperature for 20 min to remove water and oxygen under magnetic stirring, resulting in a dark brown solution. The flask was then heated to 185 °C at 10 °C min^{-1} , and maintained at this temperature for 1.5 h under Ar. When the reaction was complete, an excess of acetone was added at room temperature to form a cloudy black suspension. This suspension was separated by centrifugation at 4200 rpm for 6 min, and the black product was collected by discarding the colorless supernatant. The precipitated Rh nanocrystals were washed twice by precipitation/dissolution (re-dispersed in 7.5 ml of ethanol with sonication and then precipitated by adding 37.5 ml of hexanes).

Synthesis of Pt Nanocubes. The synthetic procedure of Pt nanocubes was the same as that used to synthesize Rh nanocubes, except that 0.1 mmol ammonium hexachloroplatinate(IV), 1.5 mmol trimethyl(tetradecyl)ammonium bromide, and 2 mmol poly(vinylpyrrolidone) were added to 20 ml ethylene glycol in a 50 ml three-necked flask at room temperature for reaction at 180 °C for 1 h.

Synthesis of Pd Nanocubes. The synthetic procedure of Pd nanocubes was the same as that used to synthesize Rh nanocubes, except that 0.1 mmol ammonium hexachloropalladate, 1.5 mmol trimethyl(tetradecyl)ammonium bromide, and 2 mmol poly(vinylpyrrolidone) were added to 20 ml ethylene glycol in a 50 ml three-necked flask at room temperature for reaction at 140 °C for 1 h.

3. Fabrication of Langmuir-Blodgett (LB) Films. Rh nanocubes were washed twice by precipitation/dissolution in chloroform (1 ml of Rh nanocrystal sol in ethanol was precipitated by adding 4 ml hexanes, and re-dispersed in 1 ml of chloroform with sonication) to further remove impurities and excess PVP. Monolayers of Rh nanocrystals were formed by placing drops of the Rh nanocrystal chloroform solution onto the water subphase of a LB trough (Nima Technology, M611) at room temperature. Surface pressure was

monitored with a Wilhelmy plate, and was adjusted to zero before spreading the nanocrystals. The resulting surface layer was compressed by moving the mobile barrier at a rate of 15 cm²/min. At a certain stage of compression, Rh monolayer at the water-air interface was carefully transferred onto continuous carbon-coated copper grids using the Langmuir-Schäffer horizontal liftoff method. Surface coverage was evaluated by counting the particles on the same area of the copper grid. Rh nanocrystals were deposited onto Si wafers (1.5 cm × 1 cm) by lift-up of the substrates at a rate of 1 mm min⁻¹ (Ref.: Zhang, Y.; Grass, M. E.; Habas, S. E.; Tao, F.; Zhang, T.; Yang, P.; Somorjai, G. A. *J. Phys. Chem. C* **2007**, *111*, 12243; Song, H.; Kim, F.; Connor, S.; Somorjai, G. A.; Yang, P. *J. Phys. Chem. B* **2005**, *109*, 188.).

4. Characterization Methods. Shape, size and lattice structure of the Rh nanocrystals were analyzed using a Philips FEI Tecnai 12 transmission electron microscope (TEM) and Philips CM200/FEG high-resolution TEM (HRTEM), operated at 100 and 200 kV, respectively. Samples were prepared by placing a drop of Rh nanocrystal sol in ethanol onto a continuous carbon-coated copper TEM grid. Powder X-ray diffraction (XRD) patterns were recorded on a Bruker D8 GADDS diffractometer using Co-K_α radiation ($\lambda = 1.79 \text{ \AA}$). Lattice parameters were calculated with the least-squares method. XPS experiments were performed on a Perkin-Elmer PHI 5300 XPS spectrometer with a position-sensitive detector and a hemispherical energy analyzer in an ion-pumped chamber (evacuated to 2×10^{-9} Torr). The Al-K_α ($BE = 1486.6 \text{ eV}$) X-ray source was operated at 300 W with 15 kV acceleration voltage. Binding energies (BE) were calibrated by setting the measured BE of C 1s to 285 eV. The atomic ratio of Rh(III/IV) to Rh(0) is fitted from Rh 3d peaks showing a standard error around 20%.

5. Pyrrole Hydrogenation. Pyrrole hydrogenation reactions were performed in a laboratory scale batch reactor with continuous gas recirculation between 30 and 70 °C. Samples were loaded into quartz reactors with a type-K thermocouple touching the reactor near the sample. Prior to the reaction, the manifold was filled with 4 Torr pyrrole (Sigma-Aldrich, >98%) and 400 Torr hydrogen (Praxair, UHP) with a balance of He (Praxair, UHP) initially at atmospheric pressure. Hydrogen and helium flows were regulated by mass flow controllers. The desired partial pressure of pyrrole was achieved by bubbling helium, assuming saturation (Ref.: Das, A.; Frenkel, M.; Gadalla, N. A. M.; Kudchadker, S.; Marsh, K. N.; Rodgers, A. S.; Wilhoit, R. C. *J. Phys. Chem. Ref. Data* **1993**, *22*(3), 659.) at room temperature and then dilution of this stream by hydrogen. Gas composition was analyzed with a HP 5890 Series II gas chromatograph (GC) equipped with a thermal conductivity (TCD) and a flame ionization (FID) detector. Turnover frequency (TOF) was calculating by extrapolating the conversion data to the initial time and by correcting the Rh surface area for coverage from TEM and SEM, and for shape (assuming non-overlapping cubic particles).

6. CO Oxidation. CO oxidation reactions were carried out similarly to the pyrrole hydrogenation reactions, but with 40 Torr CO (Praxair, UHP), 100 Torr O₂ (Praxair, UHP), and a balance of He (Praxair, UHP) initially at atmospheric pressure, all regulated by mass flow controllers. Reactions were performed between 150 and 250 °C.

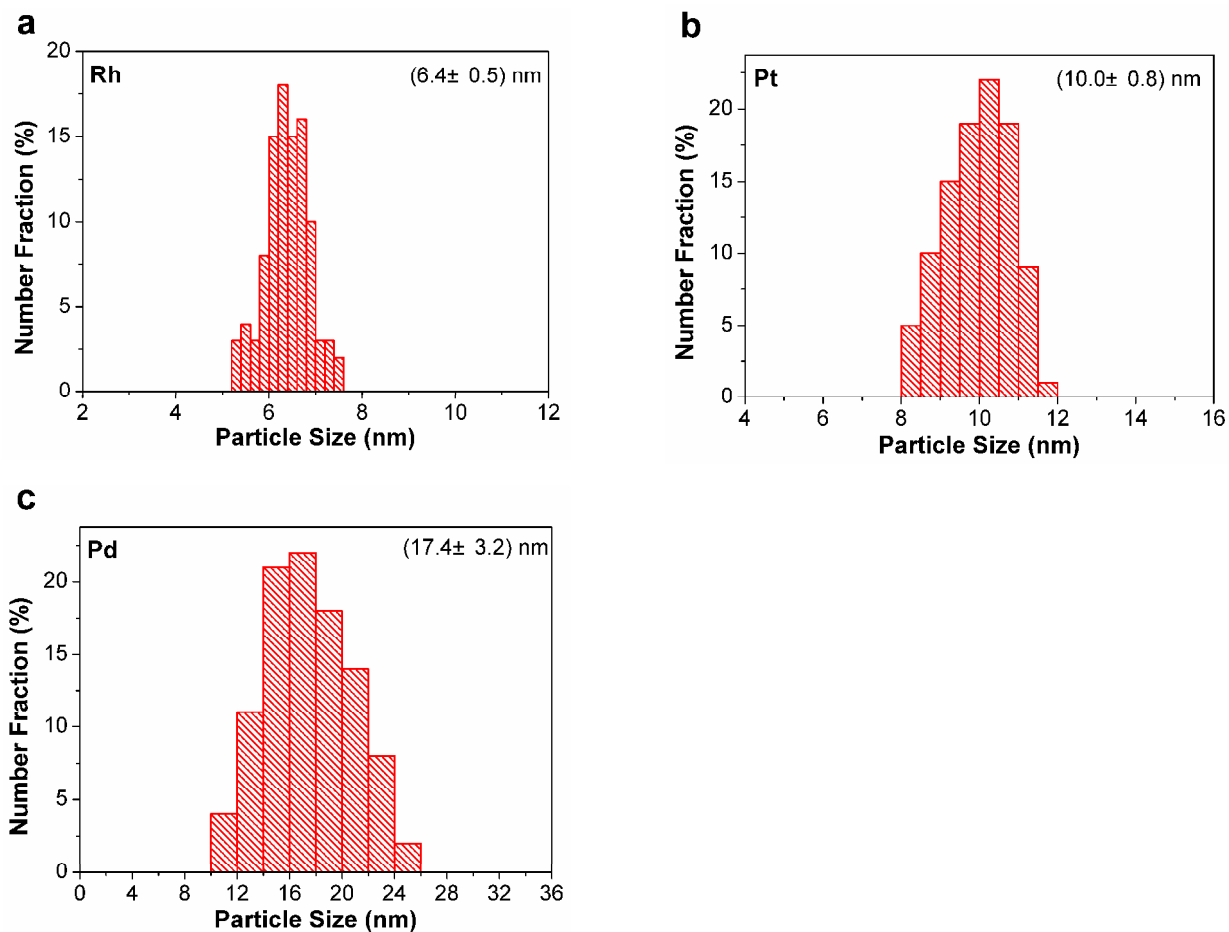


Figure S1. Size distribution histograms of as-synthesized (a) Rh, (b) Pt, and (c) Pd nanocubes.

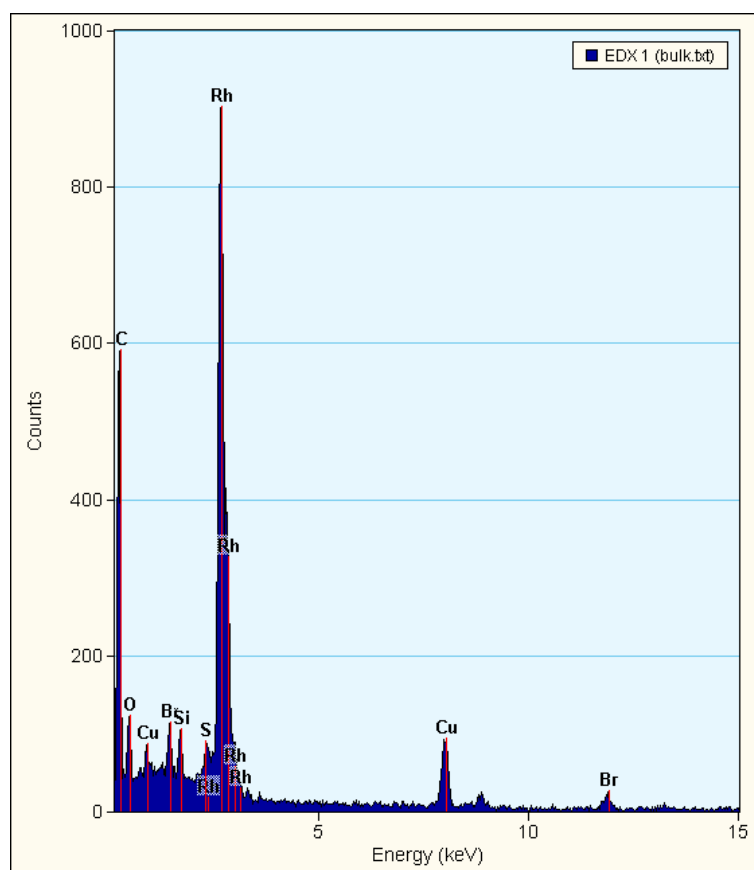


Figure S2. EDX spectrum of a large region of a TEM grid of as-synthesized Rh nanocubes. The Cu peak is

due to the TEM grid.

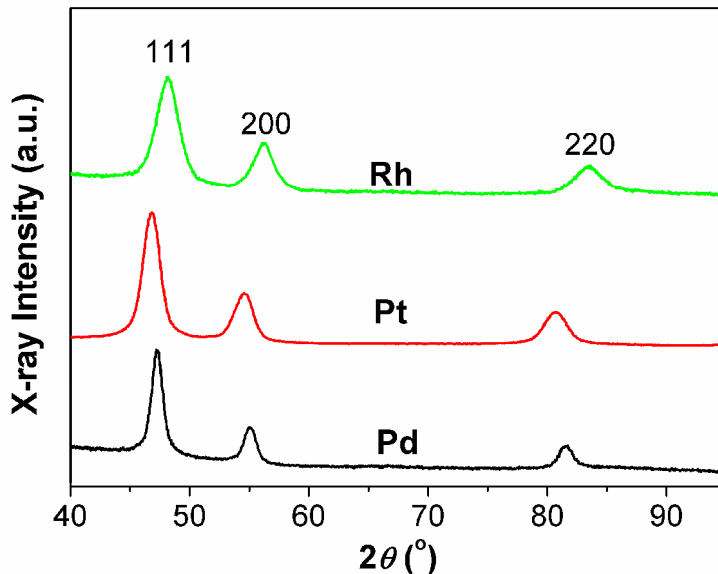


Figure S3. XRD patterns of as-synthesized Rh, Pt, and Pd nanocubes.

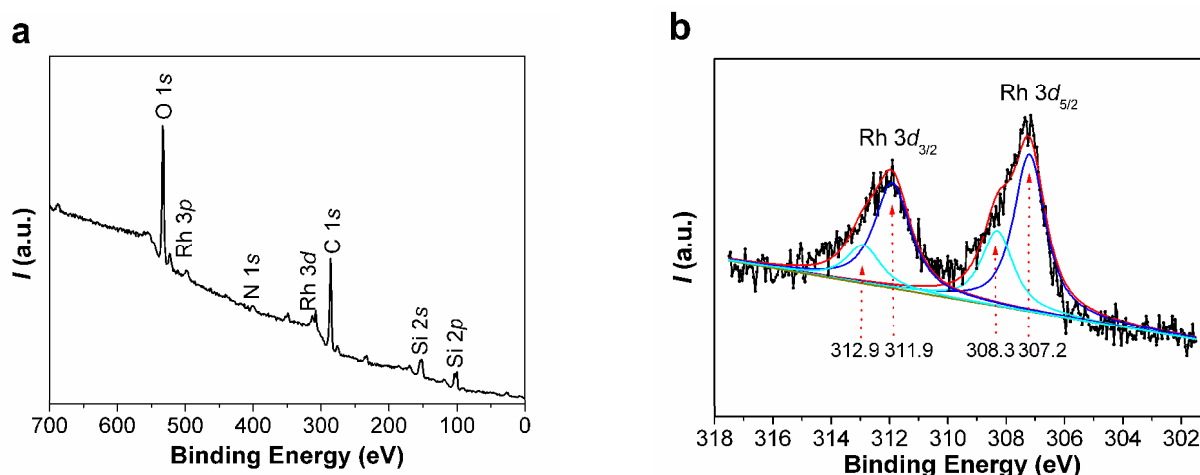


Figure S4. (a) XPS survey spectra of as-prepared Rh nanocubes deposited on a silicon wafer. (b) Rh 3d signals recorded for the Rh nanocubes.

Peaks assignable to the core levels of Rh 3p, Rh 3d, O 1s, N 1s, C 1s, Si 2s, and Si 2p are identified in Figure S4a. The weak peak of N 1s is mainly associated with the PVP and/or TTAB molecules adsorbed on the Rh nanocube surface. The Si 2s and Si 2p peaks are from the silicon wafer. The intense C 1s and O 1s peaks and the weak N 1s peak, together with the barely detectable Br 3d peak, revealed that PVP molecules were predominately adhered to the surface of the Rh nanocubes (Figure S4a). The peaks at 311.5 and 306.8 eV (Rh 3d_{3/2} and Rh 3d_{5/2}, respectively) (Figure S4b), suggest that Rh(0) is the predominant Rh species in the nanocubes (~76 at% Rh(0) and 24 at% Rh³⁺) (Ref: Abe, Y.; Kato, K.; Kawamura, M.; Sasaki, K. *Surf. Sci. Spectra* **2001**, 8, 117).

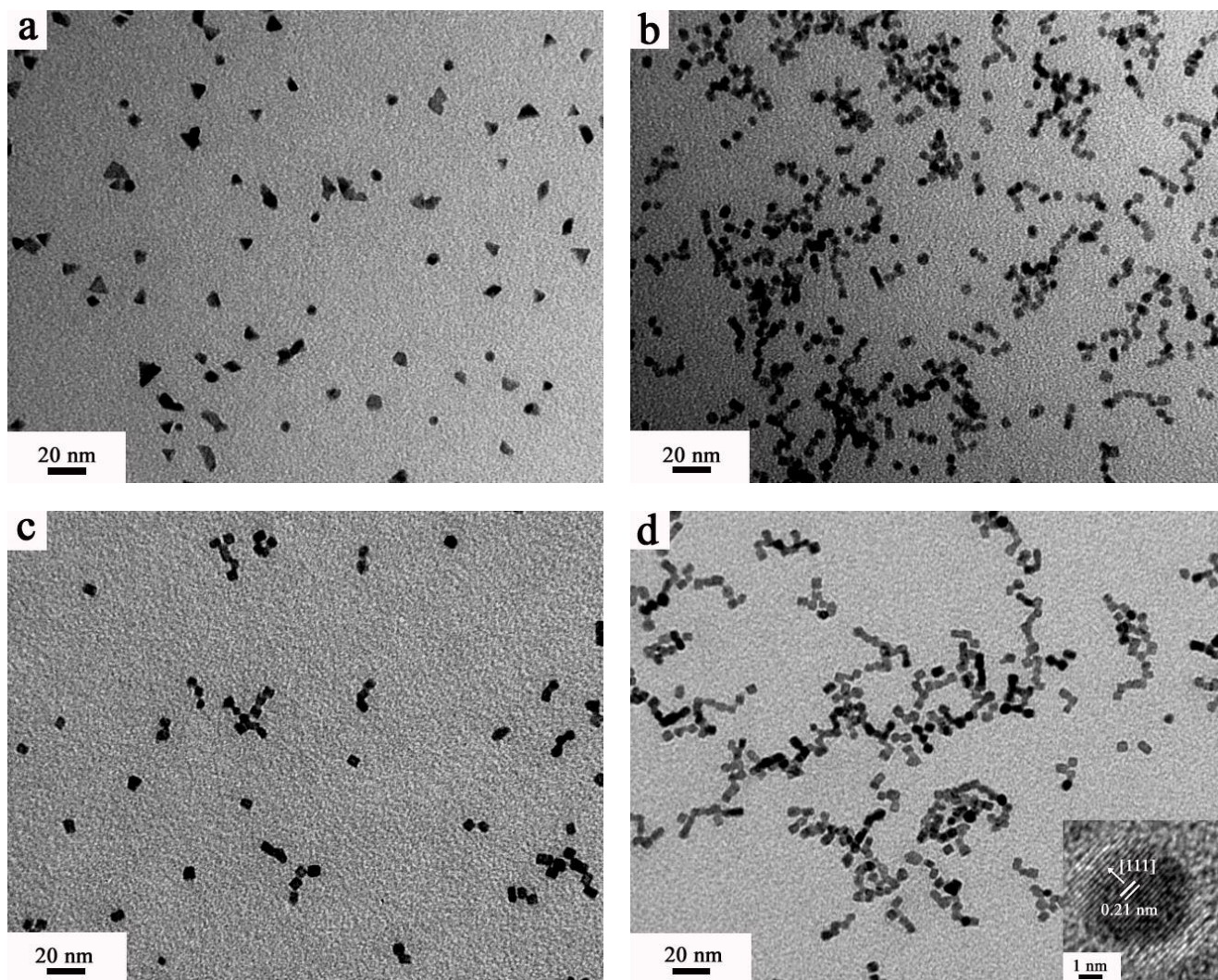


Figure S5. TEM images of Rh nanocrystals synthesized in 20 ml ethylene glycol under an Ar atmosphere: (a) 10 mM RhCl₃, 200 mM PVP, 185 °C, 1.5 h (10% cubes, 30% tetrahedra, 5.7% cuboctahedra, and 54.3% irregular particles); (b) 10 mM RhBr₃, 200 mM PVP, 185 °C, 1.5 h (40% cubes and 60% polyhedra); (c) 5 mM RhCl₃, 5 mM RhBr₃, 200 mM PVP, 185 °C, 1.5 h (39% cubes and 61% truncated cubes); (d) 10 mM RhCl₃, 10 mM TTAB, 200 mM PVP, 185 °C, 1.5 h (40% cubes and 60% truncated cubes). The inset in panel d shows a HRTEM image of a single truncated Rh nanocube enclosed by {111} and {100} faces.

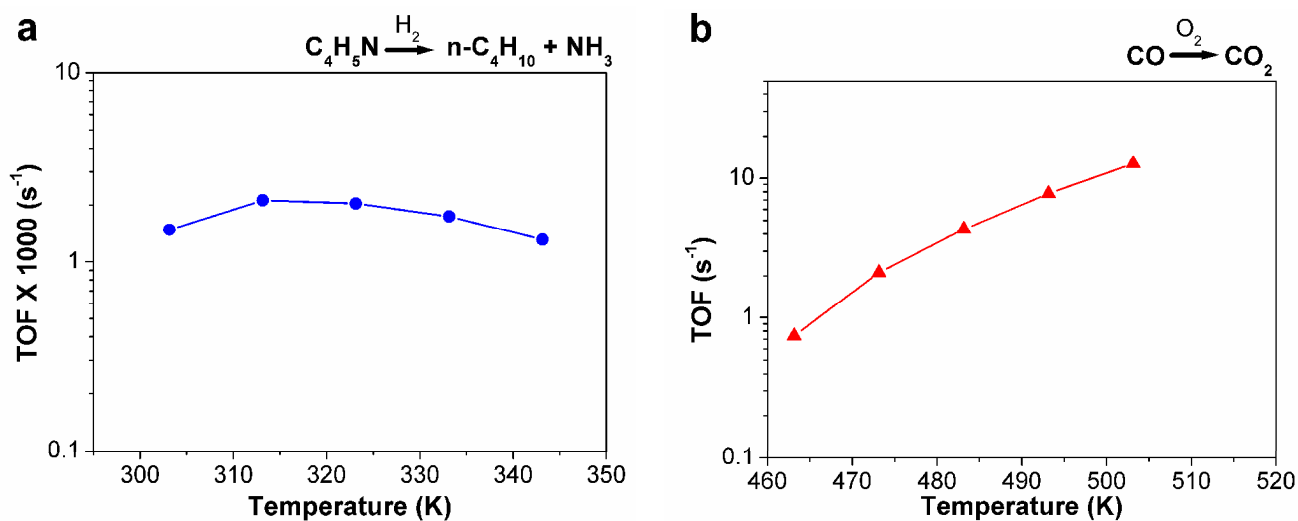


Figure S6. Turnover rate for (a) pyrrole hydrogenation to n-C₄H₁₀ and (b) CO oxidation to CO₂ for Rh nanocubes as a function of temperature.