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Supporting Information

Prominent hydrogenation catalysis of a PVP-stabilized Au_{34} superatom provided by doping a single Rh atom

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1. Experimental

1.1 Synthesis

All chemicals were commercially available and used without further purification. Au:PVP was prepared by mixing two types of aqueous solutions (**A** and **B**) using a micromixer (SIMM-V2, IMM GmbH). Solution **A** was prepared by mixing aqueous solutions of PVP with an average molecular weight of ~40 kDa (667 mg in 20 mL) and $HAuCl_4$ (30 mM, 10 mL). Solution **A** was stirred in an ice bath for 30 min. Solution **B** was prepared by adding an aqueous solution of $NaBH_4$ (56.7 mg in 5 mL) to an aqueous solution of PVP (667 mg in 25 mL), which was stirred in an ice bath for 25 min. Solution **B** was stirred for 5 min. Solutions **A** and **B** were loaded in separate plastic syringes and flowed into the micromixer at a flow rate of 200 mL/h. The eluted solution was collected and further stirred for 1 h in an ice bath and then deionized five times by using a centrifugal ultrafiltration concentrator (Vivaspin20, Vivascience) having a membrane filter with a cutoff molecular weight of 10 kDa. The deionized solution was lyophilized and Au:PVP was obtained in powder form. In the preparation of AuPd:PVP and AuRh:PVP, precursor solutions **A'** and **A"**, respectively, were used instead of solution **A**. The other procedures were the same. Solution **A'** was prepared by mixing aqueous solutions of PVP (667 mg in 20 mL), $HAuCl_4$ (30 mM, 9.7 mL) and $PdCl_2$ (30 mM, 0.3 mL). Solution **A"** was prepared by mixing aqueous solutions of PVP (667 mg in 20 mL), $HAuCl_4$ (30 mM, 9.7 mL) and $RhCl_3$ (30 mM, 0.3 mL).

1.2 Optical spectroscopy

UV-Vis absorption spectra were recorded by a spectrophotometer (V-670, Jasco).

1.3 Transmission electron microscopy (TEM)

TEM images were recorded with an electron microscope (JEM-ARM200F, Jeol) operated at 120 kV (AuPd:PVP and AuRh:PVP) or 80 kV (Au:PVP). The samples were prepared by drop casting Au clusters dispersed in methanol onto thin carbon-coated copper grids (SHR-C075, Okenshoji).

1.4 Powder X-ray diffraction (PXRD)

PXRD patterns were obtained by using a diffractometer (SmartLab 3, Rigaku) with the Cu-Kα radiation (1.5405 Å).

1.5 X-ray photoelectron spectroscopy (XPS)

XPS spectra were measured on a PHI 5000 VersaProbe (ULVAC-PHI) instrument. Binding energy was calibrated referring to the carbon 1s bands (285 eV).

1.6 Matrix-assisted laser desorption/ionization (MALDI) mass spectrometry

MALDI mass spectra were recorded by a MALDI time-of-flight mass spectrometer (AXIMA-CFR, Shimadzu) using trans-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene] malononitrile (DCTB) as a matrix. Typically, the molar ratio between Au atoms and DCTB was 1 to 8. The delay time between the pulsed laser and pulsed extraction field affected the intensity distributions of the mass spectra and was optimized for the ions with m/z ~ 6800 Da. Mass spectra were calibrated using the mass peaks of Au_n^- observed for Au:PVP. Typical mass resolution $m/\Delta m$ was 800.

1.7 X-ray absorption spectroscopy (XAS)

Rh and Pd K-edge and Au L_3-edge XAS measurements were conducted at room temperature in fluorescence mode (Rh and Pd K-edge) or transmission mode (Au L_3-edge) using the BL01B1 beamline at the SPring-8 facility of the Japan Synchrotron Radiation Research Institute. The incident X-ray beam for measurements at the Rh and Pd K-edge and Au L_3-edge was monochromatized by Si(311) (Rh and Pd K-edge) or Si(111) (Au L_3-edge) double-crystal monochromators. Data analysis was carried out by using the REX2000 software program (Rigaku). The k^3-weighted χ spectra in the k ranges of 3–14.5, 3–14 and 3–18 $Å^{-1}$ were Fourier-transformed into the r space for Rh K-, Pd K- and Au L_3-edges, respectively. In the curve-fitting analysis, the considered bonds and corresponding r range were as follows: the Rh-O, Rh-Cl and Rh-Au bonds over 1.2–2.9 Å for Rh K-edge; the Pd-Cl and Pd-Au bond over 1.6–3.0 Å for Pd K-edge; and the Au-Cl and Au-Au bonds over 1.5–3.1 Å for Au L_3-edge. All the combinations of chemical bonds were examined for fitting and only significant results are summarized in **Table S2**.

1.8 Catalytic test

Catalytic performance of Au:PVP, AuPd:PVP and AuRh:PVP in hydrogenation reactions was evaluated and compared by using 1-dodecene, styrene and cyclooctene as substrates. Reaction solutions were prepared by mixing ethanolic solutions of Au clusters (4.64 mg, 1 μmol of Au atoms, in 2 mL), additional PVP (111 mg in 2 mL) and a substrate (50 mM, 1 mL). The prepared reaction solutions were then placed in an autoclave where H_2 gas was introduced. The solutions were magnetically stirred at 800 rpm under H_2 at 303 K for 1 h. After the reactions, the solutions were analyzed by gas chromatography (GC) with naphthalene as an internal standard.

2. Results

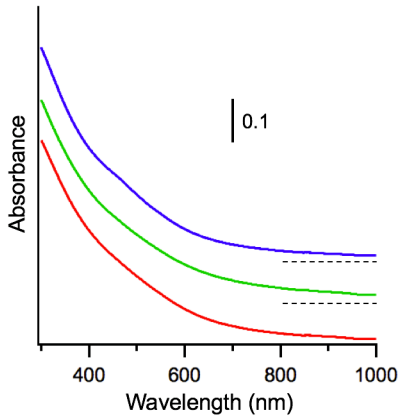

Fig. S1 UV-Vis absorption spectra of Au:PVP (blue), AuPd:PVP (green) and AuRh:PVP (red) dispersed in H_2O.

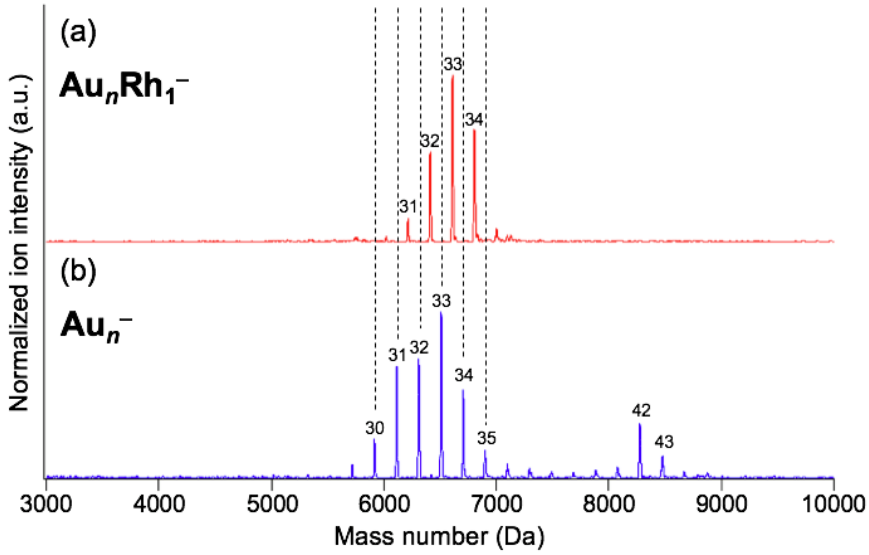

Fig. S2 MALDI mass spectra of (a) AuRh:PVP and (b) Au:PVP.

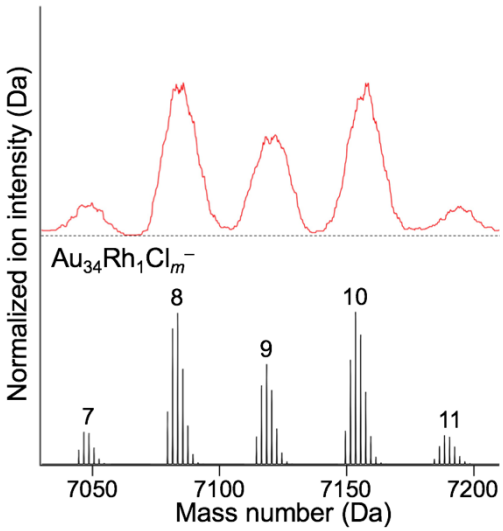

Fig. S3 Enlarged view of the MALDI mass spectrum of AuRh:PVP (red) in the region of $Au_{34}Rh_1Cl_m^-$ (m = 7-11) in **Fig. 2b** and calculated isotope patterns (black).

Table S1 Assigned clusters and mass numbers of corresponding peaks in **Fig. 2** along with calculated mass numbers.

Figure	Cluster	n	M_{exp} (Da)	M_{calc} (Da)	$M_{calc} - M_{exp}$ (Da)
2a	$Au_nRh_1^-$	31	6207	6209	2
		32	6403	6406	3
		33	6601	6603	2
		34	6799	6800	1
2b	$Au_{27}Rh_1Cl_n^-$	7	5665	5669	4
		8	5700	5705	5
		9	5736	5740	4
	$Au_{33}Rh_1Cl_n^-$	7	6850	6851	1
		8	6888	6886	-2
		9	6924	6922	-2
	$Au_{34}Rh_1Cl_n^-$	7	7049	7048	-1
		8	7084	7083	-1
		9	7120	7119	-1
		10	7157	7154	-3
		11	7194	7190	-4

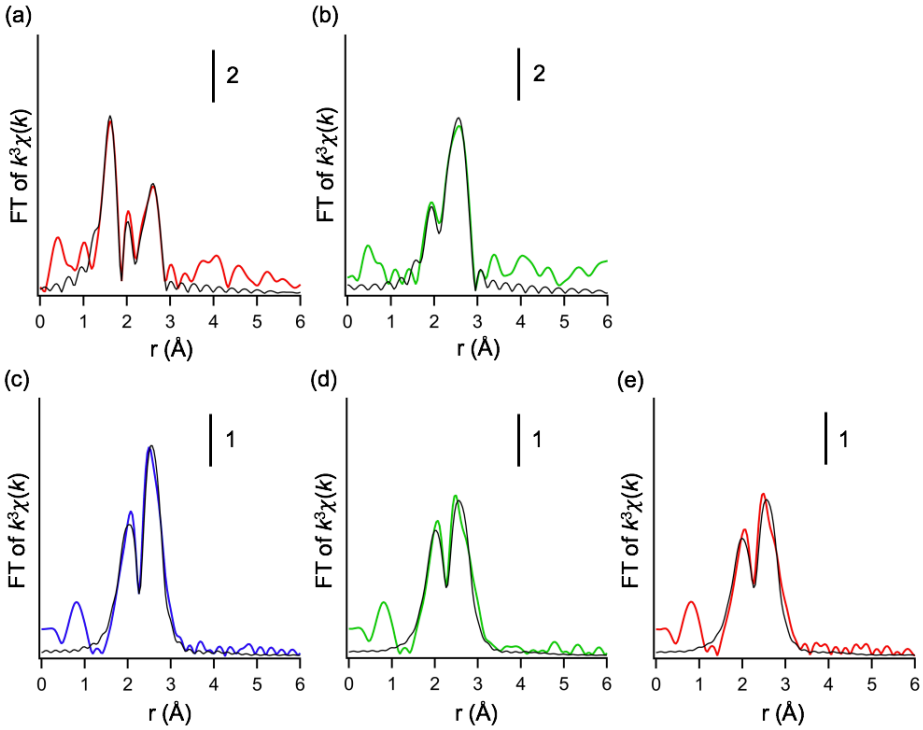

Fig. S4 FT-EXAFS spectra of (a) AuRh:PVP at Rh K-edge, (b) AuPd:PVP at Pd K-edge, and (c) Au:PVP, (d) AuPd:PVP and (e) AuRh:PVP at Au L_3-edge. Colored and black curves represent experimental and fitting results (**Table S2**) respectively.

Table S2 Structural parameters of Au:PVP, AuPd:PVP and AuRh:PVP obtained by curve-fitting analysis of FT-EXAFS spectra.

Edge	Sample	Bond	CN[a]	r (Å)[b]	σ^2 (Å^2)[c]	R (%)[d]
Rh-K	AuRh:PVP	Rh-Au	3.2(7)	2.72(1)	0.008(2)	12.0
		Rh-O	2.3(3)	2.03(1)	0.003(1)	
Pd-K	AuPd:PVP	Pd-Au	7.3(8)	2.706(2)	0.009(1)	11.5
Au-L_3	Au:PVP	Au-Au	4.3(5)	2.72(1)	0.0088(9)	11.4
		Au-Cl	0.6(2)	2.35(2)	0.008(5)	
	AuPd:PVP	Au-Au	4.4(5)	2.72(1)	0.010(1)	13.0
		Au-Cl	0.5(2)	2.35(2)	0.007(4)	
	AuRh:PVP	Au-Au	4.5(5)	2.73(1)	0.010(1)	14.7
		Au-Cl	0.6(2)	2.35(2)	0.008(5)	

[a]CN: coordination number; [b]Bond length; [c]Debye-Waller factor; [d]R is defined as $(\Sigma(k^3\chi^{data}(k)-k^3\chi^{fit}(k))^2)^{1/2}/(\Sigma(k^3\chi^{data}(k))^2)^{1/2}$.

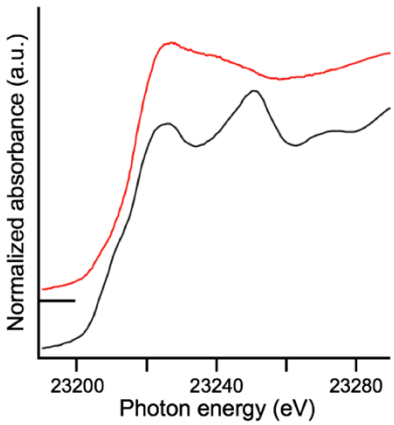

Fig. S5 Rh K-edge XANES spectra of AuRh:PVP (red) and Rh foil (black).

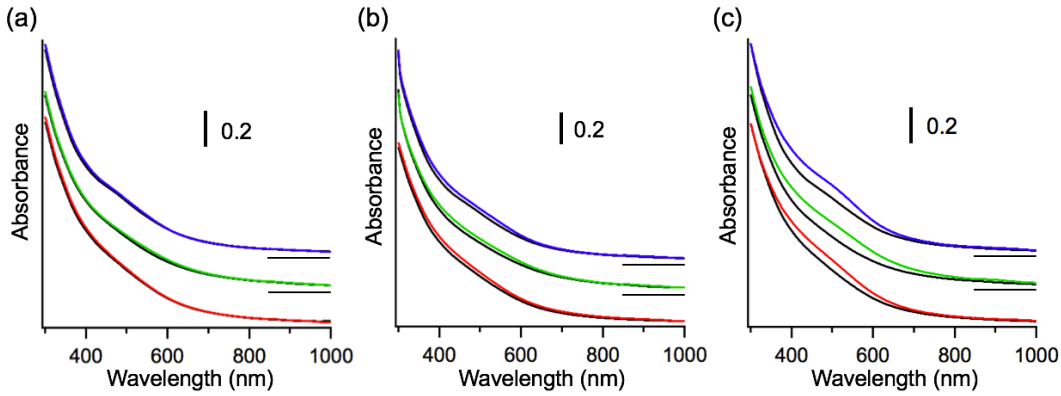

Fig. S6 UV-Vis absorption spectra of Au:PVP (blue), AuPd:PVP (green) and AuRh:PVP (red) after catalytic hydrogenation reactions of (a) 1-dodecene, (b) styrene and (c) cyclooctene. Black curves are profiles before the catalytic tests.

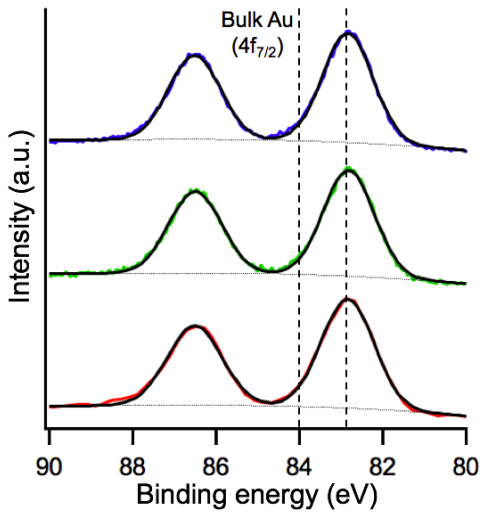

Fig. S7 X-ray photoelectron spectra of Au:PVP (blue), AuPd:PVP (green) and AuRh:PVP (red) with fitting results (black).