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Reactivity differences of Sc_NbC_@n = 68 and 80: Synthesis of the first methanofullerene derivatives of Sc_NbC_–C_n

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

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A single rhodium atom was precisely doped into a gold cluster Au$_{34}$ stabilized by poly(*N*-vinyl-2-pyrrolidone) (Au:PVP) as revealed by mass spectrometry. Rh-doped Au:PVP exhibited remarkable catalytic activity for hydrogenation reactions of olefins, which was much higher than that of recently reported Pd-doped Au:PVP.

Gold clusters stabilized by poly(*N*-vinyl-2-pyrrolidone) (Au:PVP) have provided an ideal platform for studying the correlation between structure and catalysis.[1,2] Au clusters smaller than 2 nm show excellent catalytic activity in aerobic oxidation reactions due to the negative charge on Au atoms imposed by PVP.[3-5] The activity is further improved by introducing other elements such as Ag[6,7] and Pd[8-10] owing to intracluster electron transfer to Au. For example, the catalytic activity was maximized by doping 10% and 30% of Ag[6] and Pd[10] into Au:PVP, respectively.

On the other hand, previous experimental[11,12] and theoretical[13-17] studies have demonstrated that even a single-atom dopant could dramatically change the reactivity of Au clusters. Recently, we successfully doped a single Pd atom into Au:PVP by the co-reduction method and demonstrated that AuPd:PVP thus synthesized was more reactive than undoped Au:PVP for aerobic oxidation and catalyzed chemoselective hydrogenation reactions of the C=C bonds.[18] This finding illustrates that single Pd atom doping not only enhances the oxidation catalysis of Au clusters but also provides a new catalytic ability for hydrogenation. To extend the scope of this approach, we herein doped a single Rh atom into Au:PVP as confirmed by mass spectrometry. Rh-atom-doped Au:PVP (AuRh:PVP) exhibited much higher activity than AuPd:PVP for

hydrogenation of C=C bonds.

AuRh:PVP was prepared by a procedure similar to that for AuPd:PVP.[18] An aqueous solution of HAuCl$_4$ and RhCl$_3$ with a molar ratio of 97:3 was homogeneously mixed with that of NaBH$_4$ in a microfluidic mixer[19] in the presence of PVP at 273 K. AuRh:PVP was obtained as a dark brown colloidal dispersion. As references, Au:PVP and AuPd:PVP were prepared by the reported procedure.[18,19] UV-Vis spectra of pure and doped Au:PVP showed no localized surface plasmon resonance (LSPR) band (**Fig. S1**), indicating the absence of clusters with a diameter larger than 2 nm. The average diameter of Au:PVP, AuPd:PVP and AuRh:PVP was determined to be 1.2±0.2, 1.1±0.3 and 1.3±0.3 nm, respectively, by transmission electron
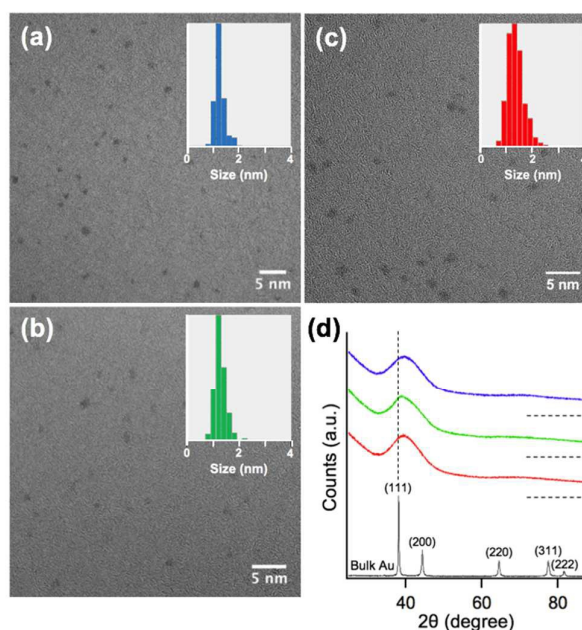

Fig. 1 TEM images of (a) Au:PVP, (b) AuPd:PVP and (c) AuRh:PVP with diameter distributions in the insets and (d) PXRD patterns of Au:PVP (blue), AuPd:PVP (green) and AuRh:PVP (red).

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microscopy (TEM) (**Fig. 1**). This result indicates that the heterometal can be doped while retaining the diameter of Au:PVP. This conclusion was also supported by the fact that the widths of the diffraction peaks corresponding to Au(111) in powder X-ray diffraction (PXRD) patterns were comparable (**Fig. 1**).

To evaluate the chemical compositions of bimetallic clusters included in AuRh:PVP, matrix-assisted laser desorption/ionization (MALDI) mass spectra were measured. **Fig. S2** compares the MALDI mass spectra of AuRh:PVP and Au:PVP recorded under high laser fluence. Only a series of $Au_nRh_1^-$ appeared in the mass spectrum of AuRh:PVP (**Fig. S2a**), whereas Au_n^- were observed in the mass spectrum of Au:PVP (**Fig. S2b**). The absence of undoped Au_n^- and overdoped $Au_nRh_m^-$ ($m \geq 2$) in the mass spectrum of AuRh:PVP revealed that the population of undoped and overdoped Au clusters was negligibly small and demonstrated that a single Rh atom was successfully introduced into each Au cluster. **Fig. 2a** shows an expanded view of the mass spectrum of AuRh:PVP in **Fig. S2a**. Although this figure suggests that $Au_{33}Rh_1^-$ is a dominant species in the sample, there is a possibility that the mass spectrum is accompanied by laser-induced dissociation. **Fig. 2b** is a typical mass spectrum recorded under minimal laser fluence to minimize dissociation during the MALDI process. We observed $Au_{34}Rh_1Cl_m^-$ as the most abundant species: although the mass peaks were not isotopically resolved (**Fig. S3**), the average mass numbers of the experimentally observed peaks agreed with those theoretically calculated within 0.1% at most (**Table S1**). Adsorption of Cl atoms originating from the synthetic precursors has also been observed in Au:PVP[20] and AuPd:PVP.[18] Based on this mass spectral data, we concluded that $Au_{34}Rh_1$ was formed as the most dominant species in AuRh:PVP. The composition is comparable to Au_{34} and $Au_{33}Pd_1$ dominant clusters contained in Au:PVP and AuPd:PVP, respectively.[18,20,21] Bare Au_{34} is a well-known magic numbered Au cluster and its magic stability has been ascribed to the closure of superatomic shells $(1S)^2(1P)^6(1D)^{10}(2S)^2(1F)^{14}$.[22,23] A variety of structures for Au_{34} such as $Au_4@Au_{30}$ with chiral

motif have been proposed based on photoelectron spectroscopy, electron diffraction, and DFT calculations.[24-31]

Interestingly, the doping modes of Rh and Pd into Au_{34} were different; a Rh atom was added to Au_{34} while a Pd atom was replaced with an Au atom in Au_{34}. The difference in the doping mode between Rh and Pd was supported by the results of Rh K- and Pd K-edge extended X-ray absorption fine structure (EXAFS) analysis. Fourier transformed EXAFS spectra are shown in **Figure S4** and structural parameters obtained by curve-fitting analysis are summarized in **Table S2**. The EXAFS data at Rh K-edge could not be fitted well only by assuming the Rh–Au bonds, whereas that at Pd K-edge could be fitted only with the Pd–Au bonds. Reasonable fitting results were obtained when we assumed coexistence of the Rh–O bonds rather than the Rh–Cl bonds. The cationic state of Rh in AuRh:PVP is supported by the Rh K-edge XANES spectrum (**Fig. S5**). The formation of the Rh–O bond(s) is ascribed to oxidation of AuRh:PVP in air. The absence of oxygen adducts in the mass spectra is probably due to the reductive dissociation of the O species during the MALDI process, since trans-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile used as a matrix is known to be an efficient electron donating matrix.[32,33] The coordination numbers (CNs) of the Rh–Au bond (3.2±0.7) at Rh K-edge was significantly smaller than that of the Pd–Au bond (7.3±0.8) at Pd K-edge. The small CN value of the Rh–Au bond and partial oxidation of the Rh dopant suggested the structure model for AuRh:PVP in which a Rh atom is attached on the surface of Au_{34}, while a Pd atom is incorporated in the surface of Au_{34} in AuPd:PVP.[18] Why was a doped Rh atom exposed on the Au cluster surface? Schaak *et al.* reported in the synthesis of Au-Rh alloy nanoparticles that the reduction of $HAuCl_4$ proceeds faster than that of $RhCl_3$.[34] This result suggests that the formation of an exposed Rh atom in AuRh:PVP is ascribed to the kinetics of the cluster formation: a Rh atom is attached onto the preformed Au_{34} cluster. In analysis of EXAFS data of AuRh:PVP and AuPd:PVP at Au-L3 edge, we did not take Au–Rh and Au–Pd bonds into consideration, because intracluster bonds are dominated by the Au–Au bonds. We included the Au–Cl bonds in the EXAFS analysis based on the mass spectral data (**Fig. 2b**). The CN values of the Au–Au bonds of the three samples (4.3–4.5) are consistent with the cluster sizes determined by mass spectrometry. Based on these results, we propose that the difference in the doping modes is attributed to whether the dopant atoms participate in the valence electron count or not: the Pd dopant contributes to the electron counting, whereas the Rh dopant does not.

Catalysis of AuRh:PVP for hydrogenation of C=C bonds was studied by using 1-dodecene, styrene and cyclooctene as model substrates. To understand the effect of single-atom doping on the catalysis, it is important to compare the catalysis under conditions in which the clusters do not decompose or aggregate. Although our previous study illustrated great improvement of the catalytic activity of AuPd:PVP over Au:PVP, UV-Vis spectroscopy suggested the aggregation of clusters during the reactions. To circumvent such problems, we added an excess amount of PVP to the reaction solution: the ratio of metal atoms to PVP monomer units was increased up to 1:1000. This simple treatment dramatically improved the stability of clusters as shown in UV-Vis spectra after the reactions (**Fig. S6**). The hydrogenation of 1-dodecene did not
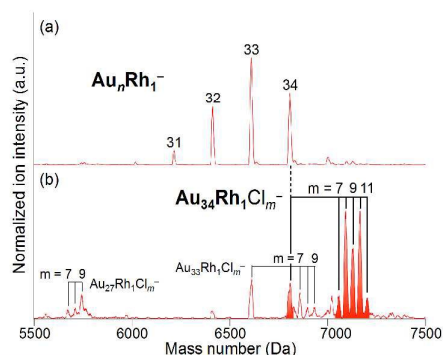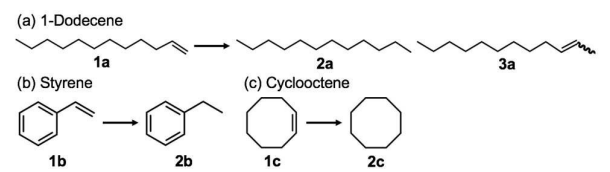

Fig. 2 MALDI mass spectra of AuRh:PVP recorded under (a) high and (b) minimal laser fluence. The most dominant $Au_{34}Rh_1$ clusters with and without Cl adducts are highlighted in (b).

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affect the spectra (**Fig. S6a**), while that of styrene and cyclooctene induced a slight change due to harsher conditions employed for the catalytic reactions (**Figs. S6b** and **c**). As shown in **Table 1**, only the doped Au:PVP could catalyze the hydrogenation reactions under mild reaction conditions. Although the synergistic effect of Au and transition metals on catalysis is well known,[35-42] these results clearly indicated that doping of even a single atom of Rh or Pd dramatically changed the reactivity of a Au_{34} superatom and led to the emergence of hydrogenation catalysis. Moreover, AuRh:PVP exhibited much higher catalytic activity than that of AuPd:PVP in all cases. These dopant effects on catalysis cannot be ascribed to the modulation of the electronic structures of Au clusters: X-ray photoelectron spectroscopy (**Fig. S7**) shows that the electronic state of Au was not affected by the doping of Rh and Pd atoms as we expected from the small doping amount. The Pd and Rh dopants act as active sites for hydrogenation and the remarkable enhancement of hydrogenation catalysis by Rh doping as compared to Pd doping is probably related to the lower coordination state of the Rh dopant. We will study the reaction mechanism in more detail including a possibility that leached species are involved (boomerang mechanism).[43,44]

Table 1 Hydrogenation reactions catalyzed by Au:PVP, AuPd:PVP and AuRh:PVP

Reaction	Dopant	H_2 (MPa)	Conversion (%)	Selectivity(**2a:3a**)
(a)	-	0.1	<1	-
	Pd		10	33:67
	Rh		90	75:25
(b)	-	0.25	1	-
	Pd		33	-
	Rh		95	-
(c)	-	0.5	<1	-
	Pd		2	-
	Rh		83	-

Reaction conditions: substrate 50 µmol; catalyst 2 at%; PVP 111 mg; ethanol 5mL; 303 K; 1h.

In summary, we succeeded in doping a single Rh atom into Au:PVP with atomic precision. MALDI mass spectrometry revealed the selective doping of a single Rh atom to a Au_{34} superatom. Rh K-edge EXAFS analysis suggested that a Rh atom is exposed on the surface of Au_{34}, which was attributed to reduction kinetics of Au and Rh precursor ions. AuRh:PVP showed much higher catalytic activity in the hydrogenation of olefins than AuPd:PVP without degradation of clusters. The much higher activity was ascribed to the lower coordination state of a Rh atom. Investigations for further insight about the origin of high catalytic activity and extension of substrate scope will be carried out in future work.

Conflicts of interest

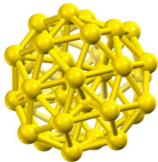There are no conflicts to declare.

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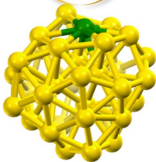
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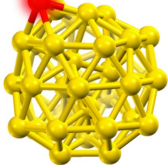
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