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Colloidal Au Single-Atom Catalysts Embedded on Pd Nanocluster

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Table S1 Preparation conditions of $Au_{55}Pd_{55}$ catalyst using various kinds of Pd NCs as mother clusters

BNCs	Pd mother clusters	Preparation conditions of Au	
		Molar ratio of starting materials	Reaction conditions
SA-S1	Pd(1h) 90°C, R_{PVP}=100	Au^{3+}/Pd =55/55, PVP/Au^{3+} =100, $C_6H_8O_6$/Au^{3+}=20/1	95°C/0.25 h
SA-S2	Pd(0.5h) 90°C, R_{PVP}=100		
SA-S3	Pd(0.25h) 90°C, R_{PVP}=100		

Table S2 Comparison between theoretical and ICP results of Pd and Au content for the $Au_{55}Pd_{55}$ catalyst prepared with various kinds of Pd NCs as mother clusters.

BNCs	Pd mother clusters	Au content in final $Au_{55}Pd_{55}$ BNCs, atomic%	
		Theoretical	ICP Au
SA-S1	Pd(1h) 90°C, R_{PVP}=100	50	49.1
SA-S2	Pd(0.5h) 90°C, R_{PVP}=100	50	47.7
SA-S3	Pd(0.25h) 90°C, R_{PVP}=100	50	48.6

Table S3 Preparation conditions of series of colloidal Au/Pd SACs with various compositions under conditions of 95°C/0.25 h by successive reduction**.**

BNCs	Pd mother clusters	Preparation conditions of Au	
		Molar ratio of starting materials	Reaction conditions
SA-1	Pd(0.25h) 90°C, R_{PVP}=100	Au^{3+}/Pd =3/55	95°C/0.25 h PVP/Au^{3+} =100/1(molar ratio), $C_6H_8O_6$/Au^{3+}=20/1(molar ratio);
SA-2		Au^{3+}/Pd =6/55	
SA-3		Au^{3+}/Pd =14/55	
SA-4		Au^{3+}/Pd =28/55	
SA-5		Au^{3+}/Pd =55/55	
SA-6		Au^{3+}/Pd =92/55	

Table S4 Comparison between theoretical and ICP results of Pd and Au content for the final Au/Pd SACs prepared with various compositions.

BNCs	Au/Pd	Au content in final Au-on-Pd catalysts, atomic%	
		Theoretical	ICP
SA-1	3/55	5.2	4.2

SA-2	6/55	9.8	7.8
SA-3	14/55	20.3	21.9
SA-4	28/55	33.7	32.1
SA-5	55/55	50.0	48.6
SA-6	92/55	62.6	60.3

Table S5 Calculated adsorption energy of Au/Pd SACs by DFT

Clusters	Calculated energy, Hartree	Spin	Crystalline facet	Adsorption energy DE, kJ/mol
Au	-18398.30535	doublet	-	-
Pd_{55}	-281493.5502	singlet	-	-
$Pd_{55}Au_6$	-391883.6299	singlet	{100}	108.5
$Pd_{55}Au_8$	-428680.5149	singlet	{111}	171.5

(In the case of $Pd_{55}Au_6$ system, for example, the adsorption energy DE was calculated by the following equation: $DE=[E(Pd_{55})+E(Au)\times6-E(Pd_{55}Au_6)]/6$.)

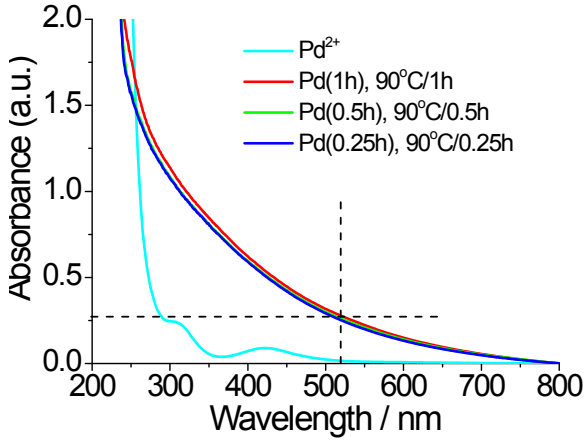
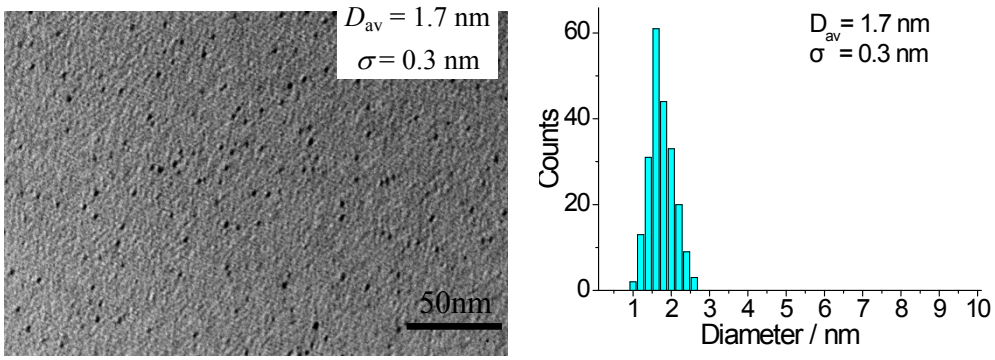
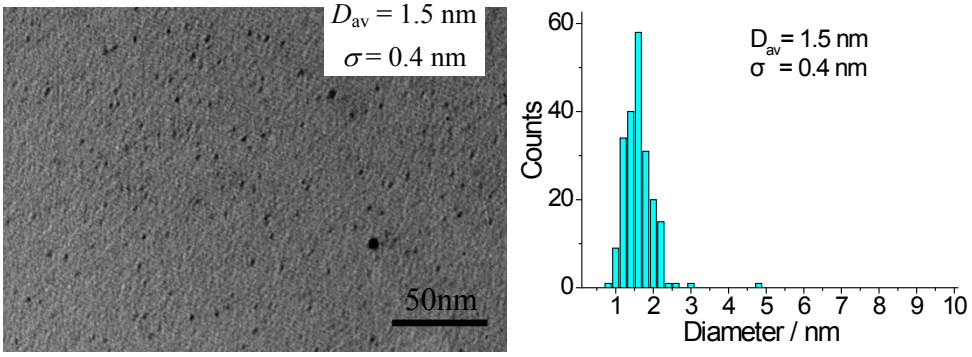


Figure S1. UV-Vis spectra of colloidal dispersions of Pd(1h), Pd(0.5h) and Pd(0.25h) mother NCs.

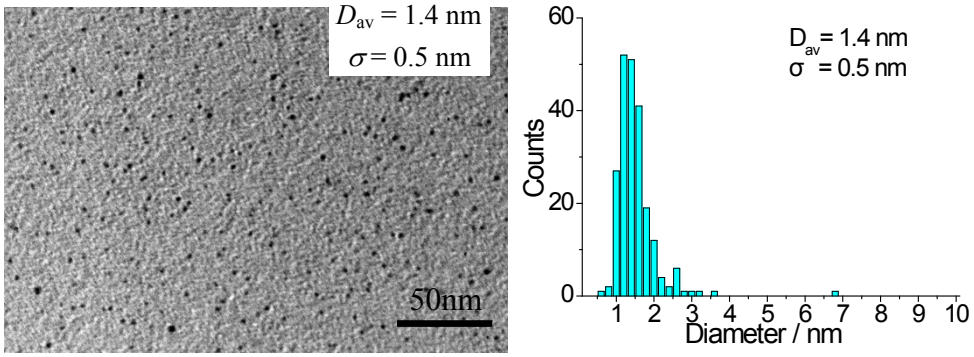
In order to get the best conditions for preparing the mother Pd NCs with tiny size, the reaction time was varied as a parameter. A series of the Pd NCs prepared were used as mother clusters for the preparation of the Au/Pd SACs. Figure S1 shows UV-Vis spectra of aqueous dispersions of Pd^{2+} ions and the Pd mother clusters prepared at 90°C for various periods. All the spectra of Pd NCs exhibit completely different shapes from that of Pd^{2+} ions and featureless and monotonously increasing absorbance toward higher energies, indicating that Pd^{2+} ions are completely reduced to Pd NCs under the present preparation conditions.



(a) Pd(1h), 90°C/1h



(b) Pd(0.5h), 90°C/0.5h



(c) Pd(0.25h), 90°C/0.25h

Figure S2. The TEM micrographs and size distribution histograms of the three kinds of Pd mother NCs prepared under 90°C for various hours.

The TEM image and size distribution histogram of the PVP-protected Pd mother NCs are shown in Figure S2. The distribution of the particle diameters of these three kinds of Pd mother clusters is nearly symmetric. The average sizes (± standard deviation) based on the TEM images (Figure S2) are 1.7 ± 0.3 nm for Pd(1h) NCs, 1.5 ± 0.4 nm for Pd(0.5h) NCs, and 1.4 ± 0.5 nm for Pd(0.25h) NCs, respectively. The results show that the average size of Pd mother clusters decrease with decreasing the reflux time. In the case of the Pd(0.25h) NCs mother clusters, the population of the PVP-protected Pd NCs has a peak at a diameter of about 1.4 nm, indicating that the Pd mother NCs consist of about 55 atoms in a particle on the average. We characterize this as the size-selected Pd_N (where N=55) NCs, where Pd_{55} is known to be a possible 'magic number' cluster [S1]. The Pd_{55} NC with the ideal size of about 1.4 nm can be characterized as a truncated octahedron with eight triangular {111} faces and six square {100} faces (Figure 1). The mean particle diameters were used for the approximate calculation and preparation of the PVP-protected colloidal Au/Pd SACs in the following steps. Here, we simply consider that all the prepared 'Pd mother clusters' possess the ideal structure of Pd_{55}, and that the defect sites including kink atoms, twinning boundaries, and

stacking faults are not taken into consideration.

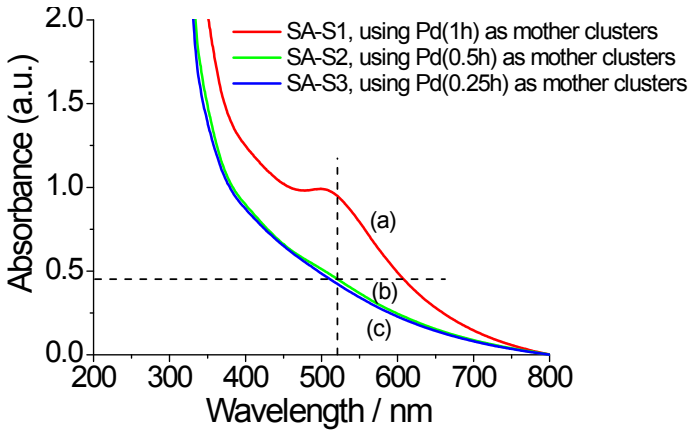
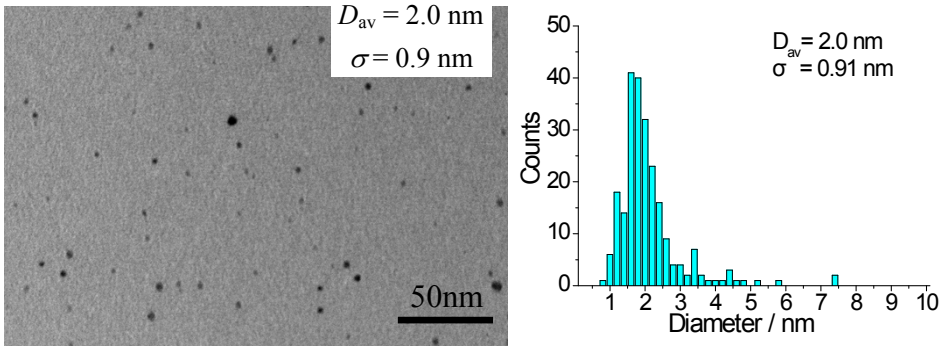


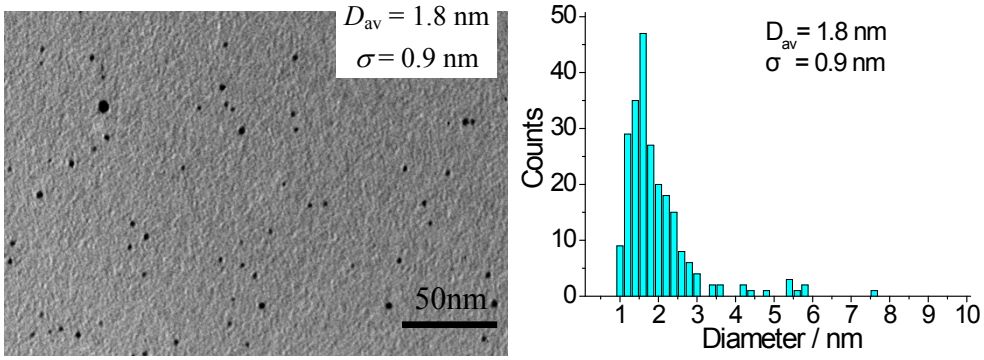
Figure S3. UV-Vis spectra of colloidal dispersions of three kinds of $Au_{55}Pd_{55}$ catalyst prepared by successive reduction using *L*-ascrobic acid as reducing reagent (Three kinds of Pd NCs of Pd(1h), Pd(0.5h) and Pd(0.25h) were used as mother clusters. All the $Au_{55}Pd_{55}$ catalysts were prepared under conditions of 95°C/0.25 hour.).

Three kinds of $Au_{55}Pd_{55}$ (the atomic ratio of Au : Pd = 55 : 55) catalysts using Pd(0.25h), Pd(0.5h), and Pd(1h) NCs, respectively, as mother clusters were synthesized at first. The UV-Vis absorption spectra of the aqueous dispersions of three kinds of $Au_{55}Pd_{55}$ catalysts are shown in Figure S3. The spectrum of the $Au_{55}Pd_{55}$ dispersion prepared from Pd(1h) NCs as mother clusters exhibits a small peak at 520 nm, attributed to the surface plasmon resonance of the metallic Au. In the case of other two series of catalysts, their spectra exhibit a featureless and monotonously increasing absorbance toward higher energies. Comparing Figure S3 with Figure S1 can give the following findings: 1) The absorbance intensities of prepared $Au_{55}Pd_{55}$ catalysts are higher than that of Pd mother NCs although the metal nanoparticle concentrations in the two dispersions are almost same, which means that the surface compositions are changed from the original Pd mother NCs, i.e. Au is deposited on the surface of Pd mother NCs. 2) It is suggested that large Pd mother NCs

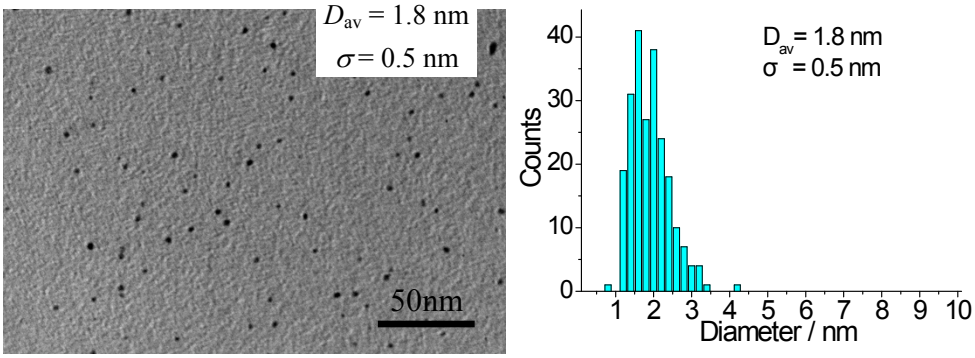
(Pd(1h)) can catch a larger amount of Au atoms, which form larger Au clusters on the surface of Pd NC (as shown in curve (a) of Figure S3). This can be explained as follows: The TEM results (Figure S4) show that the size of Pd(1h) NCs is larger than those of Pd(0.5h) and Pd(0.25h) NCs, and that, on the other hand, the ratios of Au/Pd are the same for the prepared $Au_{55}Pd_{55}$ catalysts. Thus, it is reasonably suggested that the number of Au atoms deposited on the surface of large Pd NCs (for example, Pd(1h) NCs) should be more than those of relatively small Pd NCs (Pd(0.5h) and Pd(0.25h)). It is well known that large amount of Au formed on the surface of Pd mother NCs would easily result in the aggregation of Au atoms and that the bigger aggregates could provide the stronger absorbance. Thus, the absorbance intensity of curves in Figure S3 decreases in the following order: $Au_{55}Pd(1h)_{55}$>$Au_{55}Pd(0.5h)_{55}$> $Au_{55}Pd(0.25h)_{55}$.



(a) SA-S1, using Pd(1h) as mother clusters



(b) SA-S2, using Pd(0.5h) as mother clusters



(c) SA-S3, using Pd(0.25h) as mother clusters

Figure S4. The TEM micrographs and size distribution histograms of $Au_{55}Pd_{55}$ catalysts prepared using Pd(1h), Pd(0.5h) and Pd(0.25h) as mother clusters (The $Au_{55}Pd_{55}$catalysts were synthesized using *L*-ascrobic acid as reducing reagent under conditions of 95°C/0.25 hour.).

Figure S4 shows representative TEM images and size distribution histograms of $Au_{55}Pd_{55}$ catalysts prepared with various Pd NCs as mother clusters. The average sizes (± standard deviation) of $Au_{55}Pd_{55}$ catalysts prepared by using Pd(0.25h), Pd(0.5h), and Pd(1h) NCs as mother clusters were estimated to be 1.8 ± 0.5 nm, 1.8 ± 0.9 nm, and 2.0 ± 0.9 nm, respectively, based on the TEM images, indicating that the mean particle diameter initially decreased from 2.0 nm to the smallest (1.8 nm) with decreasing the reflux time of Pd mother clusters from 1.0 to 0.25 h. Comparing Figure S4 with Figure S2, it can be found that the produced $Au_{55}Pd_{55}$ catalysts had larger average particle sizes than the corresponding Pd mother clusters, suggesting that Au atoms are indeed deposited on the surface of Pd NCs. These results are also supported by the ICP analysis of the prepared $Au_{55}Pd_{55}$ catalysts. The chemical compositions of the $Au_{55}Pd_{55}$ catalysts were obtained from the ICP analysis as shown in Table S2. Comparison of the Au atomic% in the final catalysts and that in the metal precursor feed indicates that the atomic ratio of Au in the feed in the synthetic solution was approximately equal to that in the final catalysts.

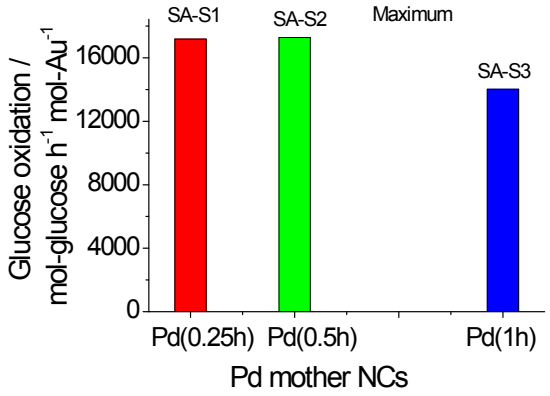


Figure S5. Catalytic activity for glucose oxidation of $Au_{55}Pd_{55}$ catalysts prepared using various kinds of Pd NCs as mother clusters. (Three kinds of Pd NCs of Pd(1h), Pd(0.5h) and Pd(0.25h) were used as mother clusters. The $Au_{55}Pd_{55}$ catalysts were prepared by successive reduction using *L*-ascrobic acid as reducing reagent under conditions of 95°C/0.25 hour.)

The prepared $Au_{55}Pd_{55}$ catalysts were used as the catalyst for the aerobic oxidation of glucose in water at 60°C. Their catalytic activity increased in the order $Au_{55}Pd(1h)_{55}$ $<Au_{55}Pd(0.5h)_{55}\approx Au_{55}Pd(0.25h)_{55}$ (Figure S5). The highest catalytic activity of about 17,200 mol-glucose·h^{-1}·mol-Au^{-1} was achieved for the smallest $Au_{55}Pd_{55}$ catalysts prepared using Pd(0.5h) and Pd(0.25h) NCs as mother clusters. The above experimental results show that $Au_{55}Pd_{55}$ catalysts with small average diameter and high catalytic activity for aerobic glucose oxidation can be obtained by using Pd(0.25h) NCs as mother clusters. The results confirm again that Au atoms would be more easily distributed on the surface of the mother clusters with small size than that with large size, which is also supported by the UV-Vis results shown in Figure S3.

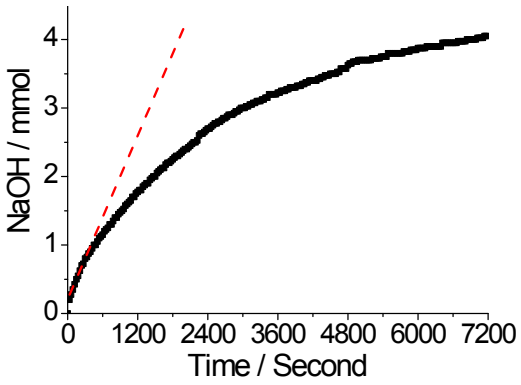
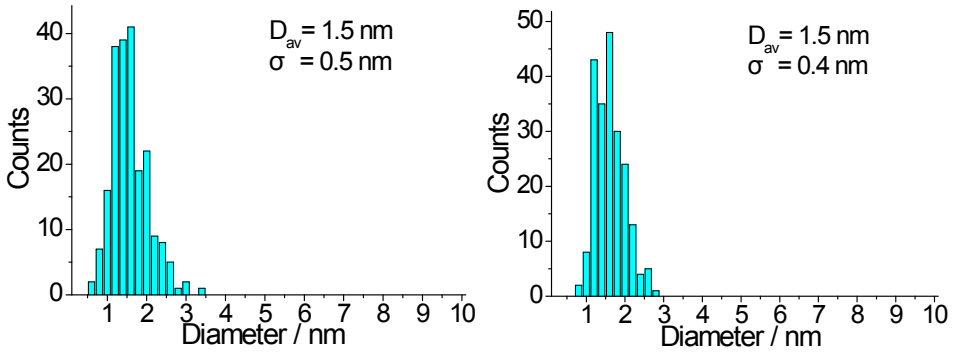
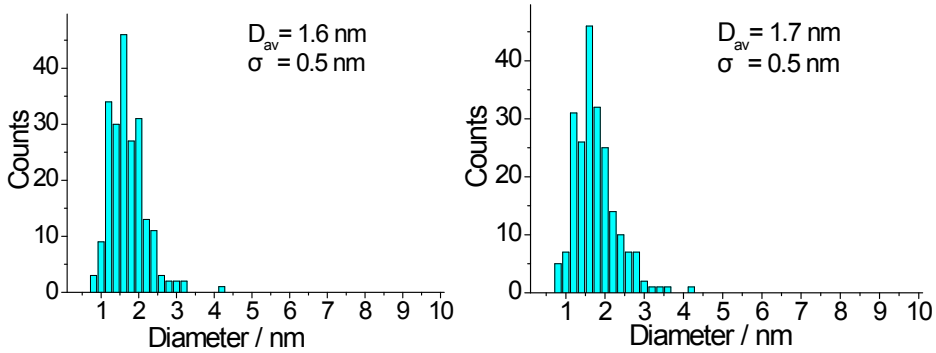


Figure S6. The typical NaOH amount vs reaction time curve for glucose oxidation catalyzed by Au_3Pd_{55} SAC. The erupting period is observed, the red das line is shown to fit the curve for determination of the simultaneous maximum activity. [glucose] / [M] ≅ 44, 400, mol ratio; pH=9.5; 60 °C.

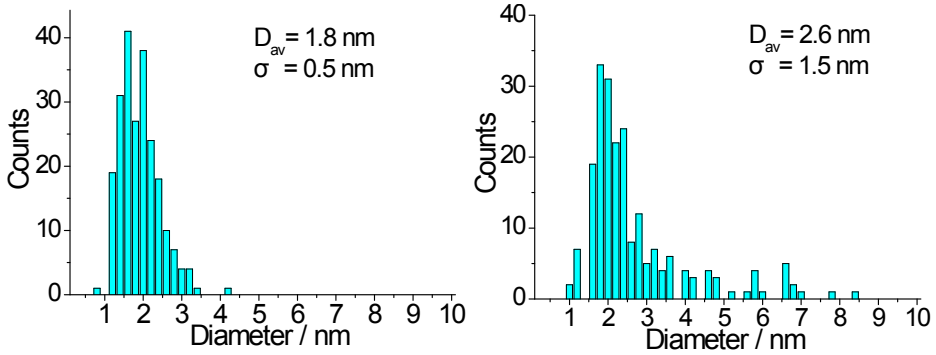
The activity (mol-glucose·h^{-1}·mol-M^{-1}) was calculated from the slope of a straight line fitted using the NaOH amount vs reaction time curve. The initial specific activity related to the metal content of the catalysts was calculated for comparison. A typical NaOH amount vs time diagram with the fit line is shown in Figure S6. The slope of the fit line reflects the initial activity of the catalyst.



(a) SA-1, Au_3Pd_{55} (b) SA-2, Au_6Pd_{55}

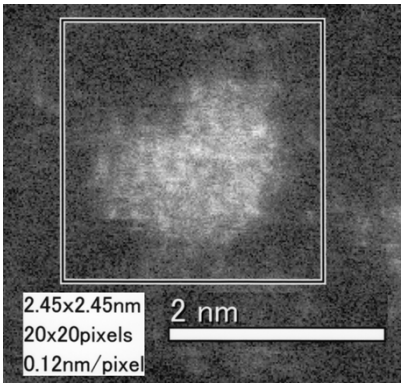


(c) SA-3, $Au_{14}Pd_{55}$ (d) SA-4, $Au_{28}Pd_{55}$

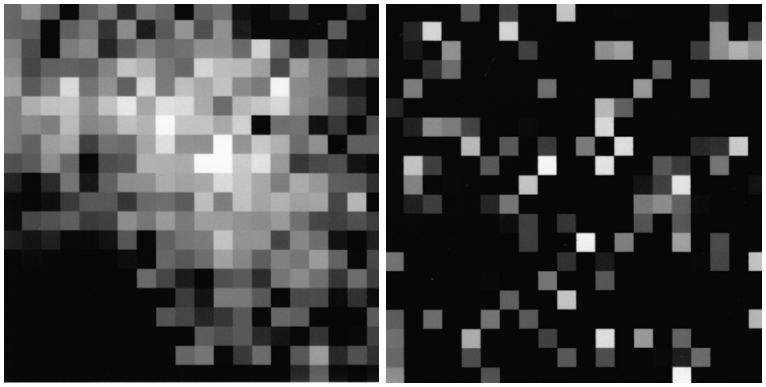


(e) SA-5, $Au_{55}Pd_{55}$ (f) SA-6, $Au_{92}Pd_{55}$

Figure S7. The size distribution histograms of colloidal Au/Pd SACs prepared with various compositions.



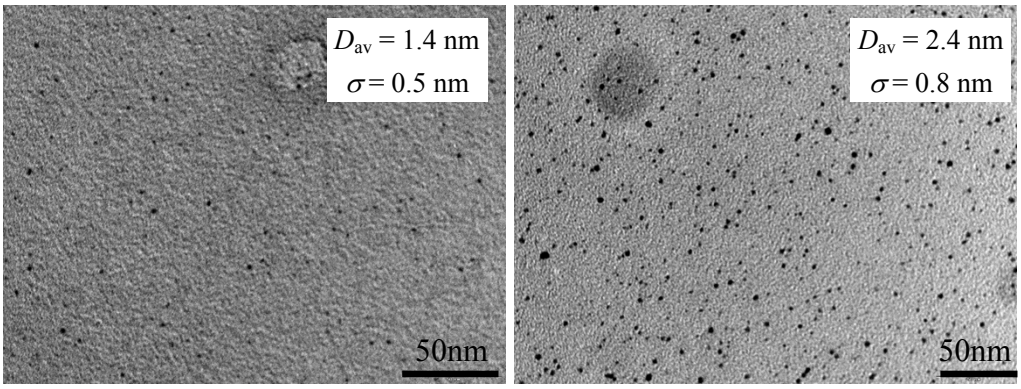
(a) HAADF-STEM of a NC of SA-1



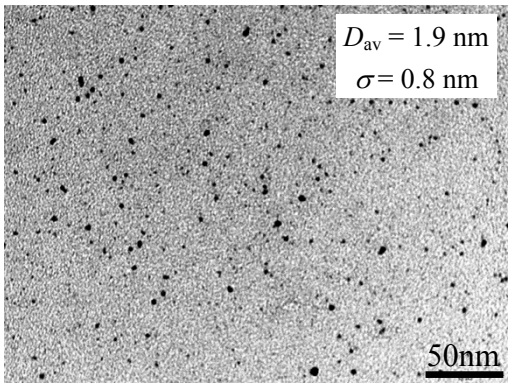
EELS of Pd EELS of Au

(b) Surface atomic configurations of a cluster of SA-1

Figure S8. HAADF-STEM image and EELS mapping of a Au_3Pd_{55} SAC NC. (a) HAADF-STEM image of a single Au_3Pd_{55} SAC NC (b) EELS mapping of a Au_3Pd_{55} SAC NC.



(a) Au NCs (b) Au/Pd (2/8) NCs



(c) Au/Pd (7/3) NCs

Figure S9. TEM micrographs and size distributions of Au NCs (a) Au/Pd (2/8) NCs (b) and Au/Pd (7/3) NCs (c) prepared by rapid injection of $NaBH_4$.

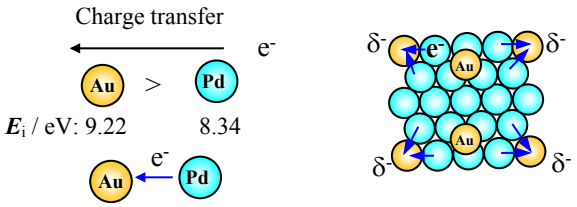


Figure S10. Schematic illustration of electronic charge transfer effects in Au_8Pd_{55} SACs (E_i: Ionization energy.).

[S1] Jongh, L. J.; Baak, J.; Brom, H. B.; Putten, D. V. D. in: P. Jena, S. N. Khanna, B. K. Rao (Eds.), Physics and chemistry of fine systems: From clusters to crystals, Kluwer, Dordrecht, 1992, vol. II, p. 839.