Supporting Information

Significant Stabilization of Palladium by Gold in the Bimetallic Nanocatalyst Leading to an Enhanced Activity in the Hydrodechlorination of Aryl Chlorides

Sangita Karanjit,[a] Atchaleeya Jinasan,[b] Ekasith Samsook,[b] Raghu N. Dhital,[a] Kenichi Motomiya,[c] Yoshinori Sato,[c,d] Kazuyuki Tohji,[c] Hidehiro Sakurai*,

[a]*Department of Applied Chemistry, Graduate School of Engineering, Osaka University 2-1 Yamada-oka, Suita, Osaka 565-0871, Japan*

[b]*NANOCAST Laboratory, Center for Catalysis Department of Chemistry and Center for Innovation in Chemistry, Faculty of Science, Mahidol University, Ratchathewi, Bangkok 10400, Thailand*

[c]*Graduate School of Environmental Studies, Tohoku University, Aoba 6-6-20, Aramaki, Aoba-ku, Sendai 980-8579, Japan*

[d]*Institute for Biomedical Sciences, Interdisciplinary Cluster for Cutting Edge Research, Shinshu University, Asahi 3-1-1, Matsumoto, 390-8621, Japan*

[e]*Japan Science and Technology Agency, ACT-C 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan*

Supporting Information

General:

All chemicals and solvents were commercially available and used without further purification. Hydrogen tetrachloroaurate tetrahydrate ($HAuCl_4.4H_2O$ Tanaka Kikinzoku), palladium chloride ($PdCl_2$, Wako), sodium tetraborohydride ($NaBH_4$, Wako) and poly (N-vinylpyrrolidone) (PVP K-30) (Kishida chemicals) were used as precursors for the preparation of monometallic and bimetallic nanoclusters. The substrates 4-Chloro-1-methoxybenzene, 1-chloro-2-methoxybenzene, 1-chloro-3-methoxybenzene, 4-chlorobenzoic acid, 1-Chloronapthalene, 2-chloronapthalene, 2-chloroanthracene, 9,10-dichloroanthracene, and bases (NaOH and KOH), solvents DMF (N,N-dimethylformamide), ethyl acetate and ether were obtained from Wako Pure Chemical Industries; Methanol, ethanol and anhydrous propan-2-ol from kanto chemicals. Milli-Q grade water was used in all experiments.

The high resolution TEM images of PVP stabilized monometallic and bimetallic gold/palladium nanoclusters (NCs) before and after reaction were recorded with a JEOL JEM-3100FE and JEM-2100F at an accelerating voltage of 300 kV and 200 kV respectively. The composition of individual metals in Au/Pd:PVP formed before and after reaction was evaluated using scanning transmission electron microscope (HITACHI, HD-2700) with an attached energy-dispersive X-ray detector (EDAX, TEAM^{TM} EDS) at 200 kV, operating in the STEM mode. GC 2010 (Shimadzu) with Rtx-5MS column length 30 m, inner diameter 0.25 mm and film thickness 0.25 μm was used for monitoring the kinetics of reactions.

Preparation of monometallic Au, Pd and bimetallic Au/Pd NCs: Monometallic Au:PVP, Pd:PVP and bimetallic Au/Pd:PVP nanoclusters were prepared by the method reported in our previous reports.[1-3] 278 mg (2.50 mmol, monomer unit of polymer) of PVP (K-30) was placed in a hard glass test tube (φ = 42 mm) and dissolved in 44 mL of Milli-Q water. Require amount of $HAuCl_4$ (from 25 mM stock solution) and $PdCl_2$ (from 12.5 mM stock solution) was added to the solution and final concentration of metal solution were made 0.5 mM (1:100 metals to polymer ratios). The resulting solution was stirred for 30 min at 27 °C. The solution was maintained 15 °C except for the case of Au NCs (at 0 °C) before reduction in organic synthesizer (EYELA, PPS-2510) and an aqueous solution (5 mL) of $NaBH_4$ (20 mg, 0.52 mmol) was added rapidly under vigorous stirring (1700 rpm). The color of the mixture was changed, indicating the formation of nanoparticle. Thus obtained Au, Pd and Au/Pd:PVP clusters were deionized subsequently by passing the colloidal solution through a membrane filter with a cut-off molecular weight of 10 kDa using a centrifugal ultrafiltration device (Vivascience, Vivaspin 20). The collected dispersion was then dried using a lyophilizer for catalytic reactions and characterizations.

General procedure for dechlorination reaction of 4-Chloro-1-methoxybenzene:
The reactions were carried out using an organic synthesizer (EYELA, PPS-2510). 4-Chloro-1-methoxybenzene (0.1 mmol) and bases NaOH or KOH (150 mol%) were placed in a test tube (φ = 15 mm). A hydrosol of Au:PVP or Pd:PVP or Au/Pd:PVP (2 atom%) in *i*-PrOH (3 ml) was added and argon was supplied from balloon without degassing the solution. The reaction was stirred vigorously (1300 rpm) at required temperature for desire time. Reaction was quenched with 1 M HCl and the mixture was extracted with ethyl acetate (3 x 10 mL). The extracts were combined, dried over Na_2SO_4 and diluted to an exact volume in a volumetric flask. The yield was determined by GC, with hexadecane as an internal standard from the calibration curve of standard solutions.

Procedure for dechlorination reaction of other Chloroarenes:
The reactions of 1-Chloro-2-methoxybenzene and 1-Chloro-3-methoxybenzene were carried out following the general procedure for dechlorination reaction of 1-Chloro-2-methoxybenzene using Au/Pd:PVP (2 atom%) at 25 °C for 5h.

4-Carboxychlorobenzene and 2,4'-dichlorobiphenyl were dechlorinated following the general procedure using 400 mol% KOH at 45 °C for 9h and 20h respectively.

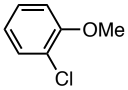
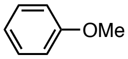
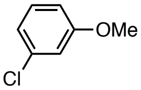
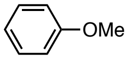
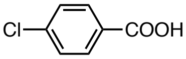
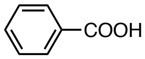
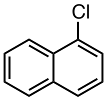
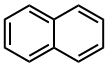
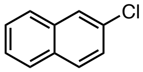
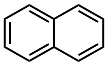
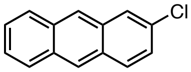
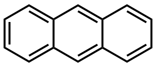
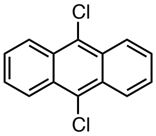
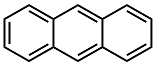
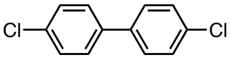
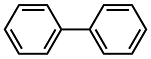
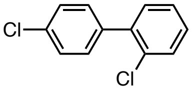
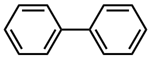
The reactions of 1-Chloronaphthalene and 2-Chloronaphthalene were performed following general procedure at 45 °C for 3h.

2-chlororoantharacene and 4,4'-dichlorobiphenyl were dechlorinated following the general procedure in 5 ml *i*-PrOH solvent at 45 °C for 15h and 8h respectively.

The reactions of 9,10-dichloroantharacene was performed following the general procedure with Au/Pd:PVP (4 atom%), 600 mol% KOH at 65 °C for 10h. The results were summarized in Table S1.

The products were confirmed by ^1H NMR spectra comparing with the pure, commercially available compounds.

Table S1. Catalytic dechlorination reaction of chloroarenes using Au/Pd:PVP catalyst

entry	substrate	product	T (°C)	t (h)	yield[a] (%)
1[b]			25	5	80
2[b]			25	5	70
3[c]			45	9	94
4			45	3	93
5			45	3	90
6[d]			45	15	95
7[f]			65	10	96
8[d]			45	8	97
9[e]			45	20	98

[a] Isolated yield. General reaction conditions: 2 atom% catalyst, 150 mol% KOH, solvent *i*-PrOH (3 mL). [b] GC yield. [c] 400 mol% KOH. [d] solvent *i*-PrOH (5 mL). [e] 400 mol% KOH. [f] 4 atom% catalyst, 600 mol% KOH, solvent *i*-PrOH (5 mL).

Figure S1 shows the effect of Au on the catalytic activity of Pd and vice versa. The dechlorination reactions of 4-Chloro-1-methoxybenzene were performed at 45 °C for 4 h under identical conditions using physical mixtures of the two monometallic catalysts Au:PVP and Pd:PVP at various Au/Pd ratios. The catalytic activity increased as compared to monometallic Au or Pd alone. Even a small amount of Pd in Au, or vice versa, enhanced the catalytic activity to a value higher than that displayed by Au or Pd alone.

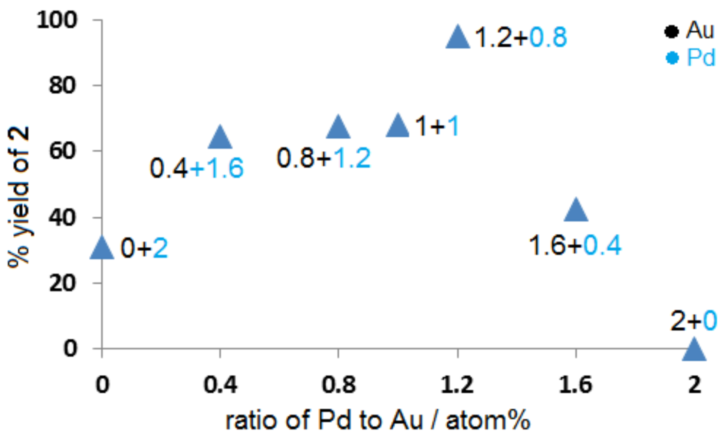


Figure S1. Relationship between catalytic activity and various Au/Pd ratios in physical mixture of Au:PVP and Pd:PVP

Kinetics of 4-Chloro-1-methoxybenzene: 0.3 mmol of **1** and 150 mol% of NaOH (0.45 mmol, 18.0 mg) were placed in a test tube (φ=30 mm). A hydrosol of Au:PVP, Pd:PVP or Au/Pd:PVP (2 atom%) in *i*-PrOH (9 ml) was added and argon was supplied from balloon without degassing the solution. The reaction was stirred vigorously (1300 rpm) at 25 °C. 0.1 mL of reaction mixture was sampled in each time intervals, then immediately quenched by 1 M HCl and extracted with ethyl acetate (0.5 mL x 3 times). GC yields of product were determined by using hexadecane as internal standard. The decay of substrate was monitored by the time dependent curve of Yield of products or decay of substrates.

Figure S2 shows the time dependent decay of 1 in the dechalorination reaction of **1** by Au/pd:PVP and plot of 1/[A] versus reaction time which show linear fit to the second order rate equation. The rate constant (k) was estimated from the slope of 1/[A] vs time, where [A] is concentration of **1**. To calculate the rate constant, initial rate of the reaction until 1 h was used.

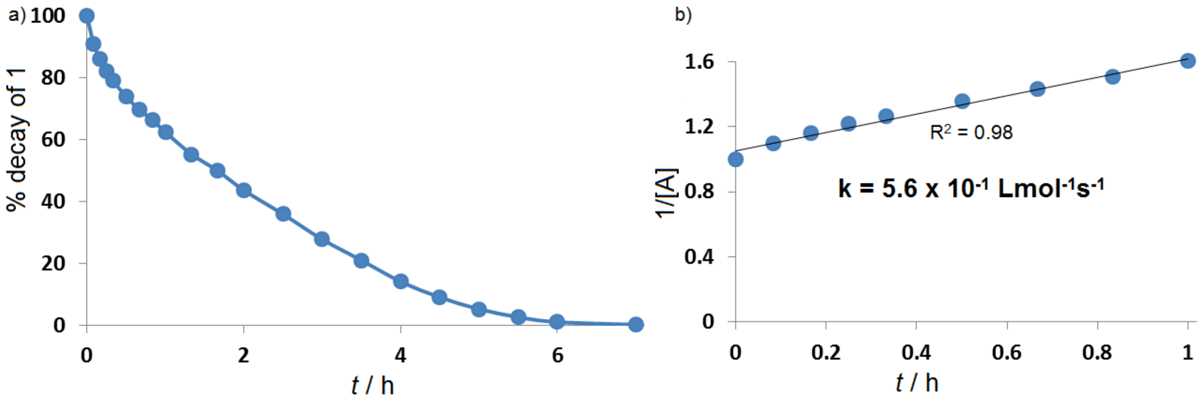


Figure S2. a) Plot of % decay of reactant **1** with time b) Plot of 1/[A] versus conversion of **1**

Characterization of catalyst before and after reaction

Two parallel sets of reaction were carried out in organic synthesizer (EYELA, PPS-2510). In one test tube (T1) (φ = 15 mm), 4-Chloro-1-methoxybenzene (0.1 mmol) and base KOH (150 mol%)

were charged. A hydrosol of Au:PVP (1 atom%) and Pd:PVP (1 atom%) in i-PrOH (3 ml) was added and argon was supplied from balloon without degassing the solution. Same process was followed for the second test tube (T2) except the substrate 4-Chloro-1-methoxybenzene. Both the reaction were stirred vigorously (1300 rpm) at 45 °C for 12 h. Then the reaction mixtures were filtered and washed by water to remove organic and inorganic compounds. Both of the catalyst after treatment was subjected to transmission electron microscopy (TEM, JEOL JEM-3100FE and JEM-2100F) and scanning transmission electron microscopy–energy dispersive X-ray spectroscopy (STEM-EDX) analysis. The sample from test tube T1 is considered as after reaction and T2 as before reaction. The scanning transmission electron microscope (HITACHI, HD-2700) attached an energy-dispersive X-ray detector (EDAX, Apolio XLT) was operated at 200 kV.

Transmission electron microscopy (TEM) analysis: A drop of aqueous catalyst from T1 and T2 were placed on the carbon coated copper gird and vacuum dried. TEM images were taken and histograms were plotted by counting more than 300 particles. The TEM images and corresponding histogram plots were shown in Figure S4. For comparison, TEM images of prepared monometallic Au:PVP, Pd:PVP and bimetallic Au/Pd:PVP were also taken and their histogram plots were also shown in Figure S3.

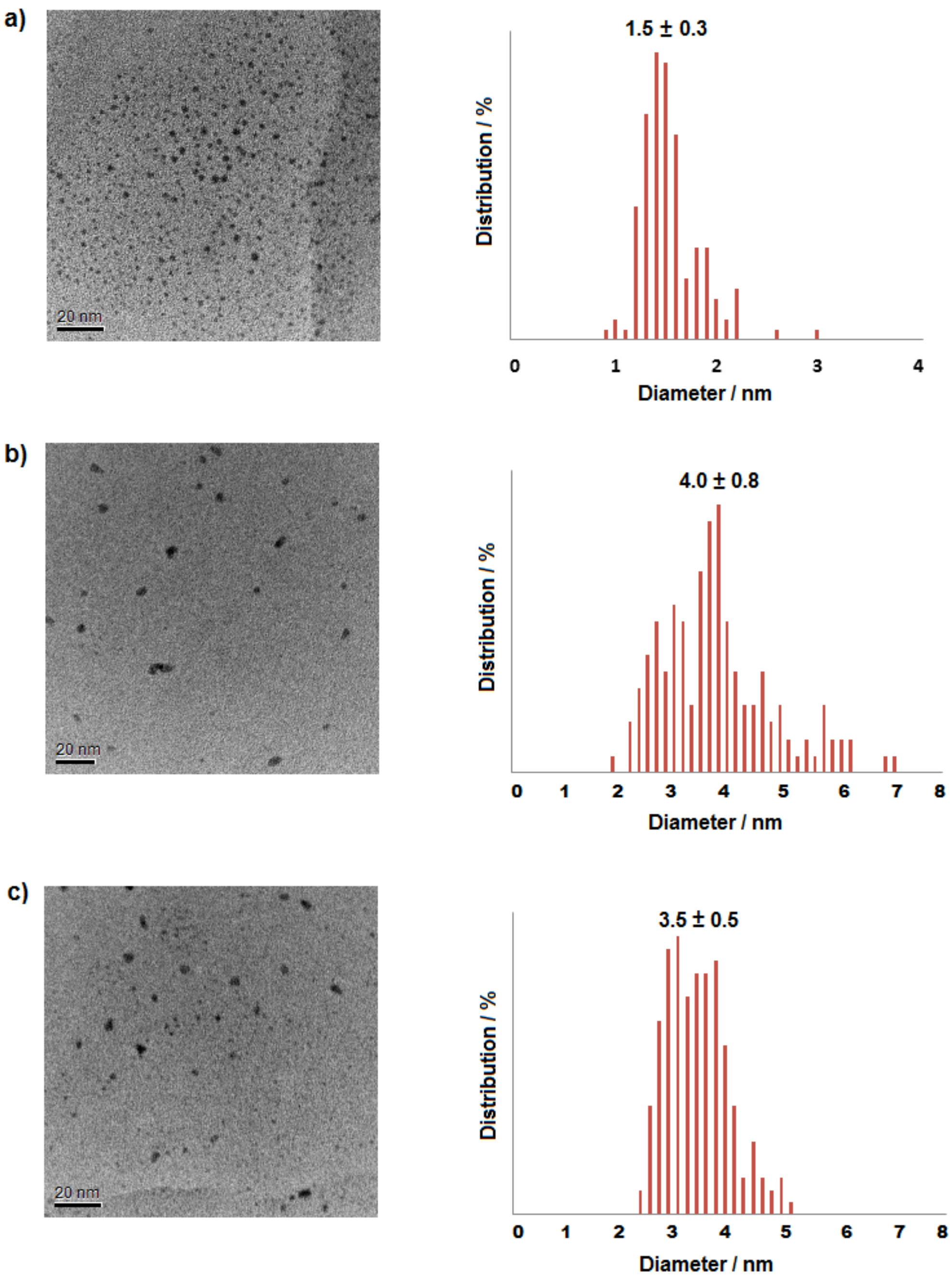


Figure S3. TEM images and the size distribution of a) Au:PVP b) Pd:PVP c) Au/Pd:PVP

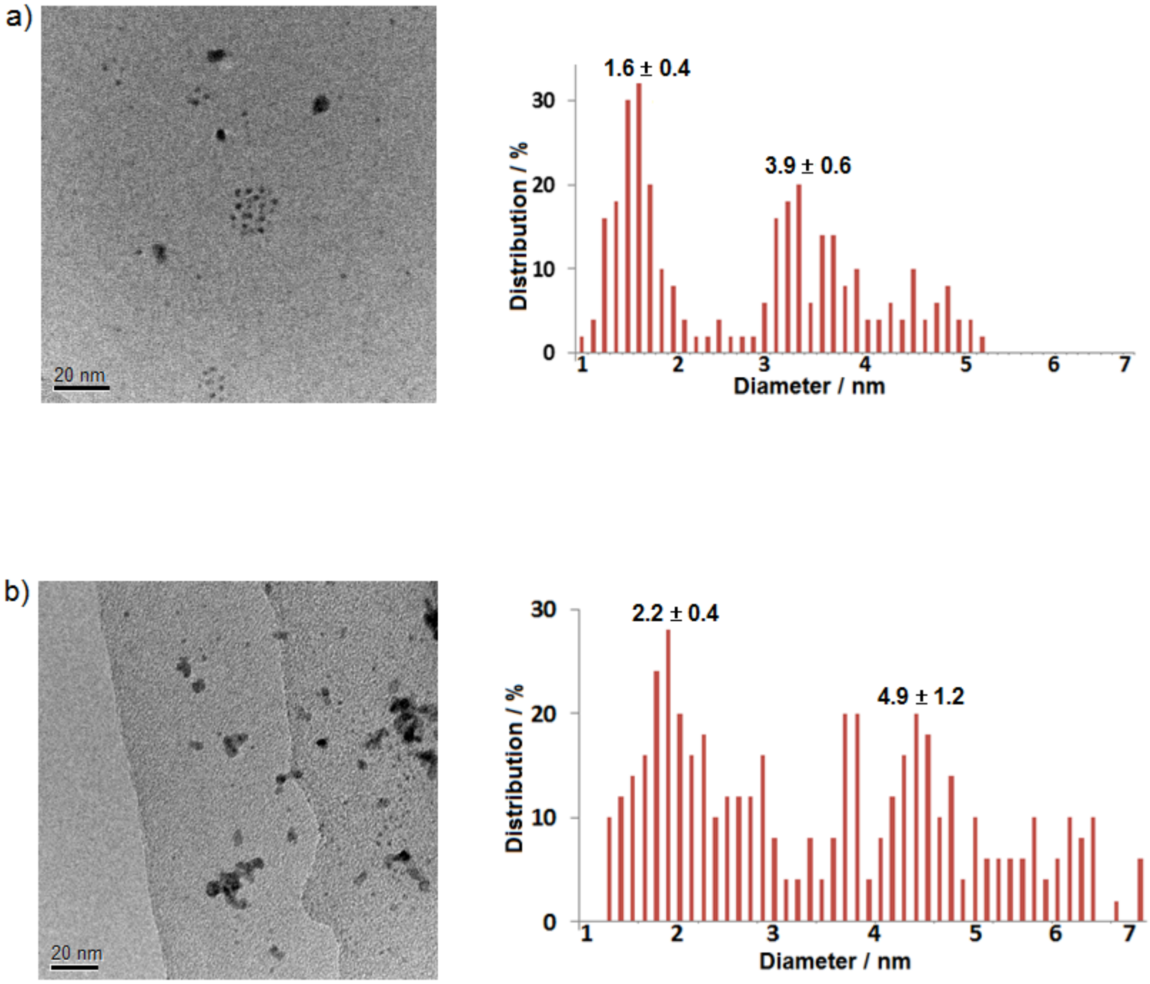


Figure S4. TEM images and size distribution of (Au+Pd):PVP a) before and b) after reaction

Particle number	Au	Pd
1	82.14	17.86
2	56.11	43.89
3	91.07	8.93
4	59.13	40.87
5	70.58	29.42

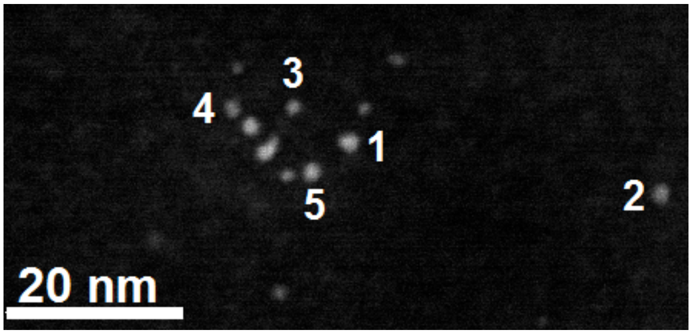


Table S2. Composition of Au/Pd bimetallic nanoparticle formed during the reaction (STEM-EDX). The particle numbers correspond to the numbers marked on the nanoparticles in the HAADF-STEM image.

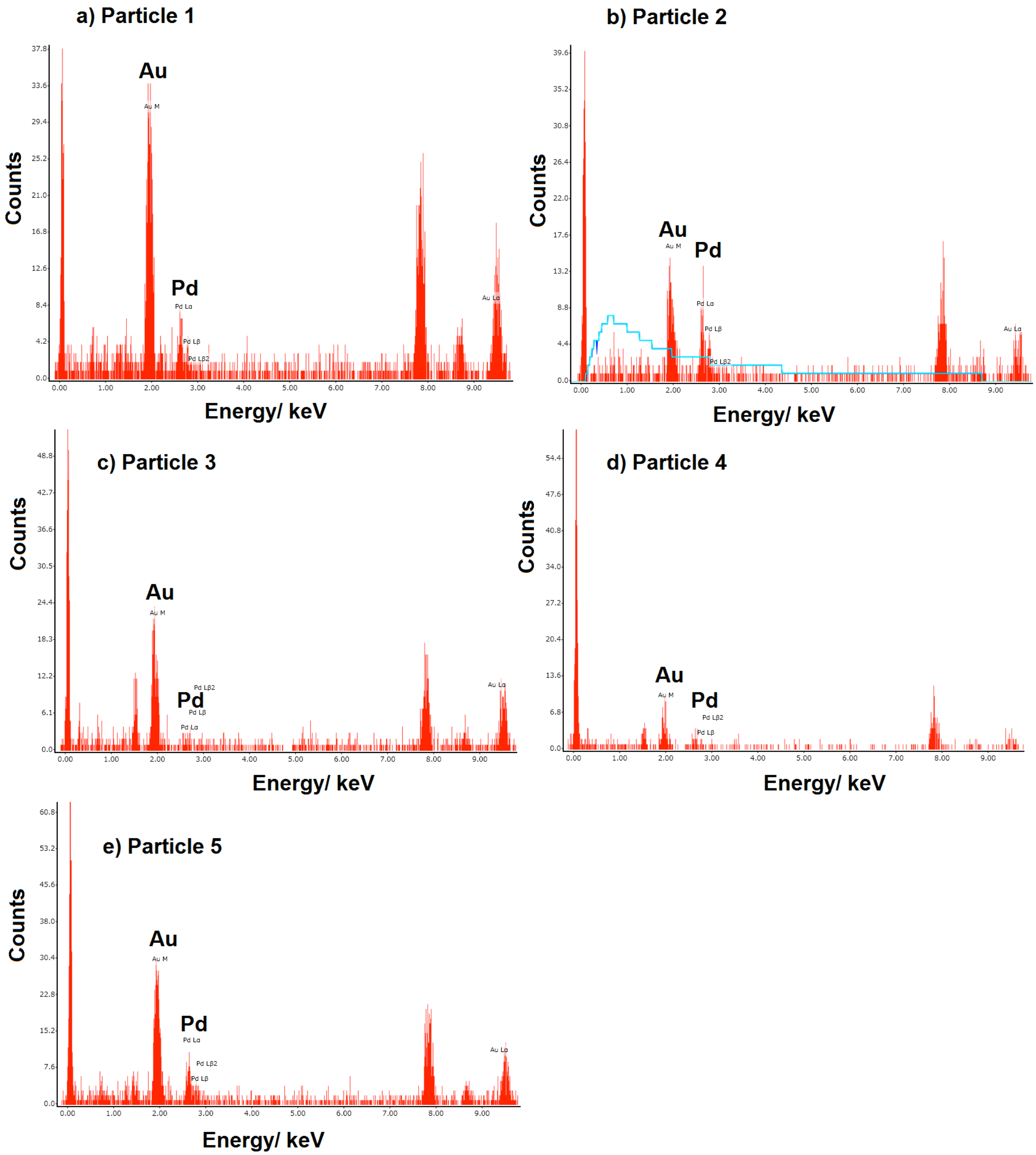


Figure S5. STEM-EDX spectra of the nanoparticles marked in the dark-field HAADF-STEM image. a) Particle 1, b) Particle 2, c) Particle 3, d) Particle 4, and e) Particle 5.

Preparation of dichlorobiphenyls:

4,4'-dichlorobiphenyl was prepared by gold catalyzed homocoupling of 4-Chlorophenylboronic acid.[1] 4-Chlorophenylboronic acid (70.2 mg, 0.45 mmol), K_2CO_3 (186.6 mg, 1.35 mmol), H_2O (15 mL) were placed in a test tube (φ = 30 mm) and Au:PVP (1 atom %) was added. The reaction mixture was stirred at room temperature under aerobic conditions for 24h. The reaction was quenched by 1 M HCl and extracted with ethyl acetate. The combined organic layer was dried over Na_2SO_4, evaporated and purified by preparative thin layer chromatography in cyclohexane. The product was analyzed by ^1H NMR which exactly matched with the reported value.[4]

2,4'-dichlorobiphenyl was prepared by $Pd(OAc)_2$ catalyzed cross coupling reaction of 1-Chloro-2-Iodobenzene and 4-chlorophenylboronic acid.[5] A mixture of Na_2CO_3 (200 mg, 2 mmol), $Pd(OAc)_2$ (1mg, 0.5 mol%), 1-Chloro-2-Iodobenzene (238.4 mg, 1 mmol), 4-chlorophenylboronic acid (234.5 mg, 1.5 mmol), 3 mL H_2O and 3 mL acetone was mixed in a test tube stirred at room temperature for 12 h. After the reaction, it was extracted with Et_2O, and combined organic layer was dried over Na_2SO_4, evaporated and purified by PTLC in dichloromethane/Hexane.

References

(1) H. Tsunoyama, H. Sakurai, N. Ichikuni, Y. Negishi, T. Tsukuda, *Langmuir,* 2004, ***20***, 11293

(2) S. S. Yudha, R. N. Dhital, H. Sakurai, *Tetrahedron Lett.,* 2011, ***52***, 2633.

(3) R. N. Dhital, C. Kamonsatikul, E. Somsook, K. Bobuatong, M. Ehara, S. Karanjit, H. Sakurai, *J. Am. Chem. Soc*., 2012, ***134***, 20250.

(4) W. Yao, W. Gong, H. Li, F. Li, J. Gaoa, J. Lang, *Dalton Trans*., 2014, ***43***, 15752.

(5) L. Liu, Y. Zhang, B. Xin, *J.Org.Chem.,* 2014, ***136***, 12245.

(6) A. Nagaki, D. Ichinari, J. Yoshida, *J. Am. Chem. Soc.,* 2014, ***136***, 12245.