Electronic Supplementary Information for Atomic-Level Pd-Au Alloying and Hydrogen-Absorption Properties in Nanoparticles Synthesized by Hydrogen Reduction

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Experimental

Synthesis:

The PVP-protected Pd nanoparticles were synthesized by stepwise growth using $PdCl_2$ as a metal precursor.S1 The obtained Pd nanoparticles were dispersed in a 200 mL of water. Then, an aqueous solution of $HAuCl_4 \cdot 3H_2O$ was added to the Pd nanoparticles suspension, and the mixture was vigorously stirred under H_2 gas for 2 hours. The Pd-Au bimetallic nanoparticles were prepared for different molar ratio of Pd nanoparticles and Au^{3+} ions (Table S1).

The protocol for the preparation of the Au nanoparticles is as follows. To an aqueous solution of $HAuCl_4$ (1 mM, 50 mL) was added 55 mg of PVP so that the molar ratio of $AuCl_4^-$ and monomer unit of PVP was kept at 1:1. The mixture was stirred for 30 min in a bath kept at 0 °C. Then, an aqueous solution of $NaBH_4$ (100 mM, 5 mL) was slowly added to the mixture under vigorous stirring. The color of the mixture immediately turned from yellow to dark red, indicating the formation of Au nanoparticles. The Au nanoparticles solution was centrifuged to remove inorganic impurities such as Na^+ and Cl^-.

Table S1 Molar ratio of Pd nanoparticles and Au^{3+} ions

Sample reference	Pd nanoparticles	$HAuCl_4 \cdot 3H_2O$	Temperature (℃)
Pd_{80}-Au_{20}	0.57 mmol	0.14 mmol	75
Pd_{50}-Au_{50}	0.57 mmol	0.57 mmol	75
Pd_{20}-Au_{80}	0.28 mmol	1.14 mmol	0

Characterisation:

HRTEM image and EDS analysis: HRTEM images and EDS analysis were performed on the JEM-2010FEF microscope with small aperture and about 1-nm electron probe size at 200 kV to analyze the distribution of Pd and Au in one Pd-Au nanoparticle. PC isotherms: The hydrogen absorption-desorption behavior of Pd, Pd-Au, and Au nanoparticles were measured from 10^{-3} up to 100 kPa of hydrogen pressure by a volumetric technique using a pressure-composition-temperature (PCT) apparatus (Suzuki Shokan Co., Ltd). Solid-state ^{2}H NMR measurement: Samples of Pd-Au nanoparticles were evacuated at 373 K for 30–60 min. After evacuation, the samples were sealed into glass capillaries with 86.7 kPa of $^{2}H_2$ gas. Solid-state 2H NMR spectra were measured at 303 K at a frequency of 61.41 MHz using a BRUKER NMR spectrometer.

1. TEM images of Pd, Pd-Au and Au nanoparticles.

Figure S1 shows TEM images and size distributions of Pd, Pd-Au and Au nanoparticles. The TEM images were taken on JEOL JEM-200CX operated at 200 kV accelerating voltage. For fluid samples, the solution was drop-cast onto a carbon-coated copper grid and allowed to dry at ambient conditions. Solid samples were transferred on TEM grid as a heterogeneous dispersion of precipitate in ethanol. The mean diameters of the Pd, Pd-Au and Au nanoparticles are listed in Table S2.

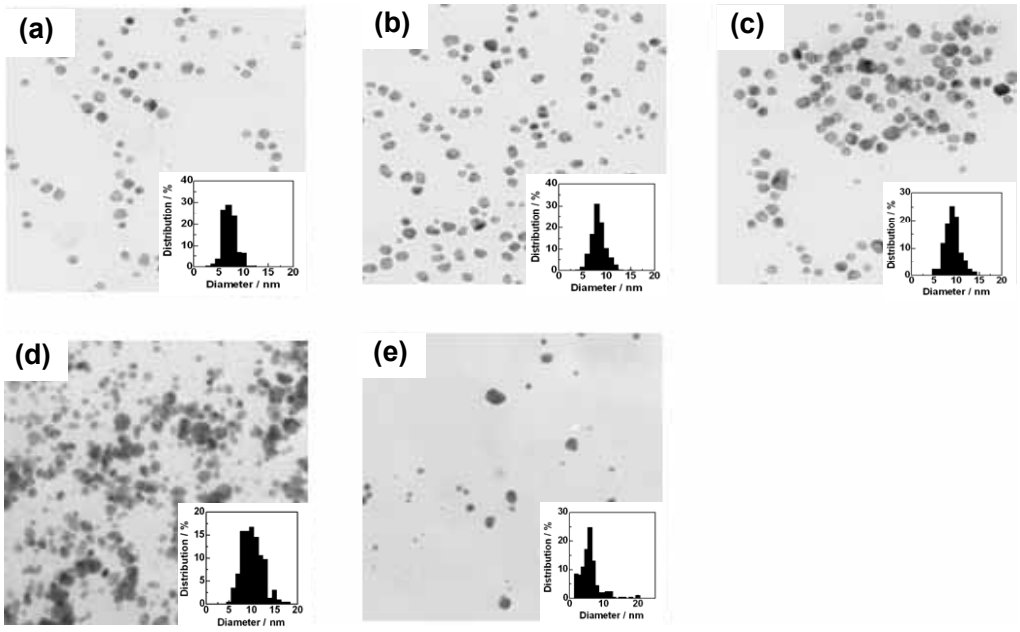

Figure S1 TEM images and size distributions of (a) 7.1 nm Pd nanoparticles, (b) 8.4 nm, (c) 9.1 nm, (d) 10.1 nm PdAu nanoparticles and (e) 6.2 nm Au nanoparticles.

Table S2 The mean diameters of Pd, Pd-Au and Au nanoparticles estimated from TEM images.

Sample reference	Diameter (nm) from TEM images
Pd	7.1 ± 1.4
Pd_{80}-Au_{20}	8.4 ± 1.6
Pd_{50}-Au_{50}	9.1 ± 1.7
Pd_{20}-Au_{80}	10.1 ± 2.3
Au	6.2 ± 2.9

2. Electronic spectra.

UV-Vis absorption spectra were measured for water suspensions of synthesized Pd-Au nanoparticles using a Jasco V-570 spectrophotometer. The UV-Vis spectra for the Pd-Au bimetallic nanoparticles showed surface plasma absorption around 530 nm for the Au and Pd_{20}-Au_{80} nanoparticles (Figure S2). On the other hand, Pd-Au nanoparticles with Au contents with 50 at% or less scarcely exhibit this absorption band, and the presence of Pd in the bimetallic nanoparticles suppresses the surface plasma energies of Au. This phenomenon is consistent with the results reported by Wu et al.,[S2] and suggesting the formation of Pd-Au bimetallic nanoparticles.

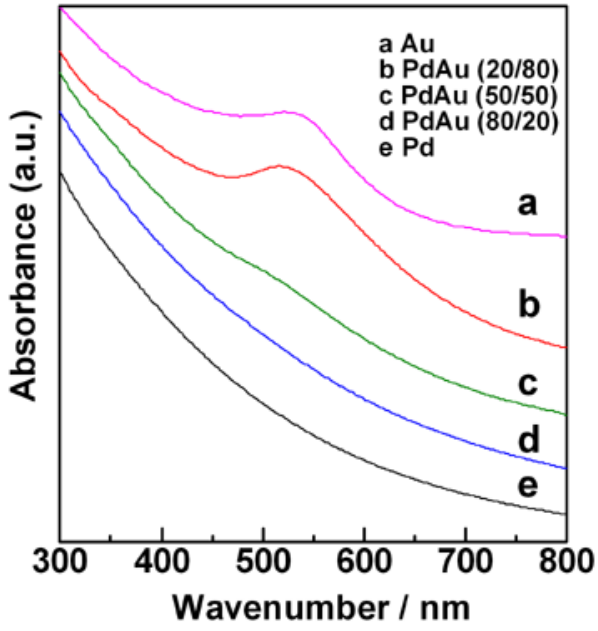

Figure S2 UV-Vis absorption spectra of Pd-Au bimetallic nanoparticles of various molar ratios.

3. The powder X-ray diffraction of Pd-Au nanoparticles

The structures of Pd and Pd-Au bimetallic nanoparticles were investigated by X-ray powder diffraction at BL-1b in KEK-PF. The wavelength is 0.6888284 (1) Å. The X-ray diffraction patterns of the samples sealed in a glass capillary under vacuum were measured at 303 K. All the XRD patterns were obtained with a 0.03° step. Figures S3 (a), (b) show the powder XRD patterns of the Pd, Au and three kinds of Pd-Au bimetallic nanoparticles. All nanoparticles showed the diffraction patterns corresponding to a single face-centered-cubic (fcc) lattice, suggesting that the structures of the obtained Pd-Au nanoparticles are solid-solution-type where Pd and Au are mixed at atomic level. The lattice constants and the crystal sizes of Pd, Au and three kinds of Pd-Au bimetallic nanoparticles were determined by pattern-fitting analysis based on Le Bail, and are shown in Figure S3(c) and Table S1, respectively. The lattice constants of Pd-Au nanoparticles increase with Au contents.

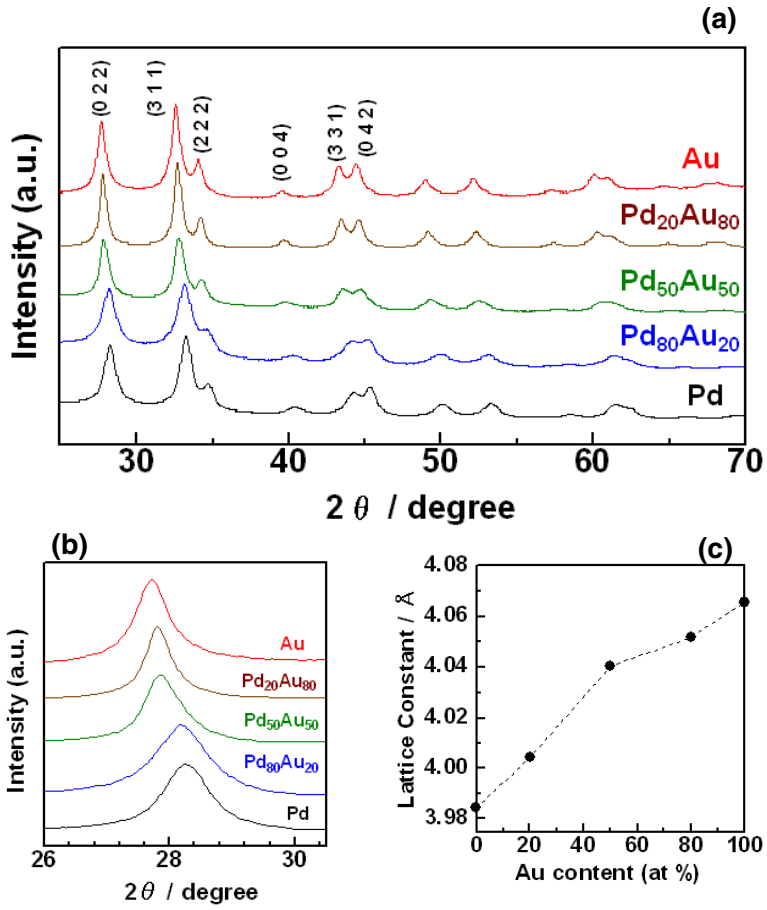

Figure S3 Powder XRD patterns of Pd/Au nanoparticles. The 2θ ranges from 25.0° to 70.0° (a) and 26.0° to 30.5° (b). The lattice constants were estimated by Le Bail fitting to the diffraction patterns (c).

4. Schematic view of the density of states (DOS) near the Fermi level in Pd-Au nanoparticles

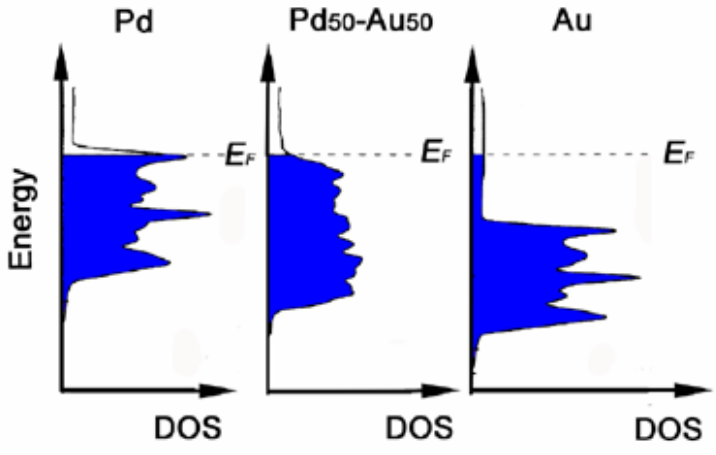

Figure S4 Schematic view of DOS near the Fermi level in Pd-Au nanoparticles

References.

[S1] Teranishi, T.; Miyake, M. Chem. Mater. 1998, 10, 594-600.

[S2] Wu, M.-L.; Chen, D.-H.; Huang, T.-C. *Langmuir* **2001**, *17*, 3877-3883.