Supporting Information

Hydrogen-Storage Properties of Solid-Solution Alloys of Immiscible Elements

Neighboring Pd

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1. Experimental details

Syntheses of $\text{Ag}_x\text{Rh}_{100-x}$ Nanoparticles: In a typical synthesis of Ag–Rh nanoparticles, poly(vinyl pyrrolidone) (PVP, 111 mg, MW $\approx$ 40 000, Wako) was dissolved in ethylene glycol (200 ml) and the solution heated to 170°C in air under magnetic stirring. Meanwhile, AgNO_3 (8.4 mg, 0.050 mmol, Kishida) and $\text{Rh}(\text{CH}_3\text{COO})_3$ (14.1 mg, 0.050 mmol, Mitsuwa) were co-dissolved in deionized water (20 ml). The aqueous solution of AgNO_3 and $\text{Rh}(\text{CH}_3\text{COO})_3$ was then added to the ethylene glycol. Other $\text{Ag}_x\text{Rh}_{1-x}$ ($x = 40$ and 60) nanoparticles were prepared by controlling the molar ratio of Ag^+ and Rh^{3+} ions. For $\text{Ag}_{40}\text{Rh}_{60}$ nanoparticles, AgNO_3 (4.2 mg, 0.025 mmol) and $\text{Rh}(\text{CH}_3\text{COO})_3$ (20.9 mg, 0.075 mmol) were co-dissolved in deionized water (20 ml). For $\text{Ag}_{70}\text{Rh}_{30}$ nanoparticles, AgNO_3 (12.8 mg, 0.075 mmol) and $\text{Rh}(\text{CH}_3\text{COO})_3$ (7.0 mg, 0.025 mmol) were co-dissolved in deionized water (20 ml).

Characterization: The particle compositions were determined using AAS and EDX techniques (see SI 1). TEM images were captured using a JEOL JEM-2000EX TEM operated at 200 kV. HRSTEM, HAADF-STEM and EDX analyses were recorded with a HITACHI HD-2700 STEM operated at 200 kV at the Naka Application Center, Hitachi High-Technologies Corporation. AAS analysis was carried out using a SHIMADZU AA-6300. Synchrotron XRD patterns were measured at the beam line BL02B2, SPring-8. Pressure-composition isotherms were measured by a pressure-composition-temperature apparatus (Suzuki Shokan Co., Ltd). Solid-state ^2H NMR spectra were recorded at 303 K in a fixed magnetic field of 94 kOe and a frequency sweep of 60.94–61.94 MHz, using a BRUKER NMR spectrometer.

2. Particle composition

Compositions of the particles were determined using atomic absorption spectrophotometric (AAS) and energy-dispersive X-ray (EDX) techniques. Results obtained from the two techniques were very similar for all metallic compositions (**Table S1**).

Table S1. Results of the particle composition of Ag–Rh bimetallic nanoparticles

AAS results	EDX results
Ag ₄₀ Rh ₆₀	Ag ₃₈ Rh ₆₂
Ag ₅₁ Rh ₄₉	Ag ₄₉ Rh ₅₁
Ag ₆₆ Rh ₃₄	Ag ₆₉ Rh ₃₁

3. TEM images and size distributions of $\text{Ag}_x\text{Rh}_{1-x}$ nanoparticles

TEM images were recorded on a JEOL JEM-2000EX or JEM-200CX, operated at 200 kV accelerating voltage. The samples dispersed with ethanol were drop-cast onto a carbon-coated copper grid and allowed to dry under ambient conditions. The mean diameters of the nanoparticles were determined from the TEM images to be **a)** 10.2 ± 1.0 , **b)** 12.2 ± 1.6 , and **c)** 13.6 ± 1.5 , respectively. Numbers that follow the $\pm$ sign represent estimated standard deviations.

Figure S1. TEM images and the size distributions of **a), d), g)** $\text{Ag}_{40}\text{Rh}_{60}$, **b), e), h)** $\text{Ag}_{50}\text{Rh}_{50}$, and **c), f), i)** $\text{Ag}_{70}\text{Rh}_{30}$.

4. Line scanning analysis of a $\text{Ag}_{50}\text{Rh}_{50}$ nanoparticle

The line-scan was correlated with the physical position of the nanoparticle as denoted by the white line in the inset of Figure S2. The compositional line profiles of Ag and Rh on a $\text{Ag}_{50}\text{Rh}_{50}$ nanoparticle indicate that an atomic-level Ag–Rh alloying occurs without significant segregation of each metal component.

Figure S2. Compositional line profiles of Ag and Rh from a $\text{Ag}_{50}\text{Rh}_{50}$ alloy nanoparticle recorded along the line shown in the STEM image (inset). Ag–L and Rh–L refer to the L electron shells of the Ag and Rh atoms, respectively. The profiles were obtained by plotting the integrated intensities at the Ag L–shell and Rh L–shell ionization edges.

5. Electronic spectra

UV-Vis absorption spectra were measured for ethanol suspensions of $\text{Ag}_x\text{Rh}_{1-x}$ nanoparticles using a Jasco V-570 spectrophotometer. The Ag–Rh nanoparticles (Ag : Rh = 70 : 30 and 50 : 50) showed a broad band, in contrast to a sharp band for Ag nanoparticles and a continuous curve for Ag–Rh nanoparticles (Ag : Rh = 40 : 60) and Rh nanoparticles. The surface plasmon peak observed in the solid-solution alloys continuously decrease with increasing Rh content. This is caused by a continuous change of the Ag electronic state in the solid-solution Ag–Rh, indicating the formation of Ag–Rh solid-solution nanoparticles.

Figure S3. UV-Vis absorption spectra of Ag–Rh bimetallic nanoparticles at various molar ratios.

6. XPS spectra

XPS spectra for samples on an carbon sheet were recorded on a Physical Electronics PHI 5800 ESCA system with a background pressure of approximately 1×10^{-9} Torr. The binding energies were corrected by reference to the C(1s) line at 284.5 eV. Figure S4 shows Ag 3d and Rh 3d core level XPS of samples. The values of Ag 3d and Rh 3d binding energies are summarized in Table S2. In Ag 3d, spectral shift is different from the general shifts.^(S1) If silver is oxidized, the binding energy is shifted to lower energy. In Figure S4, Ag 3d binding energies of alloys shifted continuously to the lower energy with increasing Rh content, which is in agreement with the oxidization of Ag. In contrast, Rh 3d binding energies of alloys shifted continuously to the lower energy with increasing Ag content, which is in agreement with the reduction of Rh. Thus the electronic structures of Rh and Ag are approached each other by the solid-solution alloying.

(S1) Kaushik, V. K. *J. Electron Spectrosc. Relat. Phenom.* **1991**, 56, 273-277.

Figure S4. The Ag 3d and Rh 3d core-level XPS of Ag_xRh_{100-x} nanoparticles.

Table S2. The binding energy of the Ag 3d and Rh 3d

Sample	BE(Ag 3d_{3/2}) (eV)	BE(Ag 3d_{5/2}) (eV)	BE(Rh 3d_{3/2}) (eV)	BE(Rh 3d_{5/2}) (eV)
Rh			311.57	306.79
Ag ₄₀ Rh ₆₀	372.85	366.87	311.25	306.39
Ag ₅₀ Rh ₅₀	373.16	367.17	311.14	306.35
Ag ₇₀ Rh ₃₀	373.32	367.30	311.14	306.36
Ag	373.38	367.39		