

Chapter 2

Hydrogen Storage Properties of Solid Solution Alloys of Immiscible Neighboring Elements with Pd

2.1 Introduction

Atomic-level (solid solution) alloying has the advantage of being able to continuously control chemical and physical properties of elements by changing compositions and/or combinations of constituent elements [1–3]. However, solid solution phases in alloys are limited to specific combinations of elements. Furthermore, most of the combinations have solid solution phases in limited regions of composition and temperature. Thus, alloys often undergo phase separation from the high-temperature solid solution state when the temperature is reduced. Even in such cases, we can obtain solid solution phases at room temperature as a metastable state using a quenching technique from the high-temperature solid solution phase. However, in certain cases, the constituent elements are immiscible even in a high-temperature liquid phase. In such cases, solid solution phases have not yet been obtained, because the quenching technique is not applicable to the phase-separated liquid phase.

Rh, Pd and Ag are neighboring noble metals in the 4d transition-metal series. Each is well known as an effective catalyst for various chemical reactions [4–7]. If these metals could be mixed in a desired ratio, then their chemical and physical properties could be enhanced. In the Ag–Pd solid solution system that has complete solid solubility, the hydrogen permeability is most enhanced when the ratio is Ag:Pd = 24:76. The thin film resulting from this system is used as a hydrogen-permeable membrane [8]. However, in the other two combinations, namely Pd–Rh and Ag–Rh, phase separation occurs, with complete insolubility at room temperature [9, 10]. In the case of Ag–Rh, even in the liquid phase at around 2,000 °C, Ag and Rh do not mix, and segregated clustering of each element forms. Considering the band-filling effect in the III–V semiconductors, [11] the Ag_{0.5}Rh_{0.5} solid solution alloy is expected to have a similar electronic structure to Pd and resemble Pd in terms of chemical and physical properties, since Pd is located between Rh and Ag in the periodic table. For example, one of the well-known unique properties of

Pd is its hydrogen storage property, which is attributed to its electronic structure; [12–15] Rh and Ag have no hydrogen storage ability. Does the $\text{Ag}_{0.5}\text{Rh}_{0.5}$ solid solution alloy actually absorb hydrogen? In this chapter, the author reports the first example of a AgRh solid solution alloy exhibiting a hydrogen storage property.

Recently, several techniques for stabilizing nonequilibrium phase at ordinary temperatures and pressures have been attracting attention. Changing the size of a particle to the nanometer scale appears to be a particularly efficient technique. For example, various nonequilibrium solid solution alloys such as Au–Pt, Au–Ni, Au–Fe and Ag–Pt, which exist in solid solution at high temperature or in the liquid phase, have been easily obtained as metal nanoparticles by solution chemistry methods [16–23]. This may allow the isolation of novel solid solution alloys even in the entirely immiscible Ag–Rh system.

2.2 Experiment

2.2.1 Syntheses of $\text{Ag}_x\text{Rh}_{1-x}$ Nanoparticles

In a typical synthesis of AgRh nanoparticles, poly(*N*-vinyl-2-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 $\text{Ag}_x\text{Rh}_{1-x}$ ($x = 0.4$ and 0.7) nanoparticles were prepared by controlling the molar ratio of Ag^+ and Rh^{3+} ions. For $\text{Ag}_{0.4}\text{Rh}_{0.6}$ 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 $\text{Ag}_{0.7}\text{Rh}_{0.3}$ 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).

2.2.2 Characterizations

Transmission Electron Microscopy Analysis

Transmission Electron Microscopy (TEM) images were recorded on a JEOL JEM-2000EX TEM instrument operated at 200 kV accelerate voltage. The samples dispersed with ethanol were drop-cast onto a carbon-coated copper grid and allowed to dry under ambient conditions.

Synchrotron X-Ray Diffraction Measurement

Synchrotron XRD patterns were measured at the beam line BL02B2, SPring-8. The diffraction patterns of the samples sealed in glass capillaries under vacuum were measured at 303 K. The wavelength is $\lambda = 0.55277 \text{ \AA}$.

Atomic Absorption Spectrophotometric Measurement

AAS analysis was carried out with a SHIMADZU AA-6300 using samples dissolved in nitric acid solution.

Scanning Transmission Electron Microscopy Analysis

High resolution (HR) STEM, high-angle annular dark-field (HAADF) STEM and energy-dispersive X-ray (EDX) analyses were recorded on a HITACHI HD-2700 STEM operated at 200 kV accelerate voltage at the Naka Application Center, Hitachi High-Technologies Corporation.

UV-Vis Spectra Measurement

UV-vis absorption spectra were measured for ethanol suspensions of $\text{Ag}_x\text{Rh}_{1-x}$ nanoparticles using a Jasco V-570 spectrophotometer.

In Situ XRD Measurement

The thermal stability of $\text{Ag}_{0.5}\text{Rh}_{0.5}$ nanoparticles was investigated by in situ powder XRD analysis measured at the BL02B2 beamline, SPring-8. The XRD patterns of the samples sealed in a glass capillary were measured in situ under vacuum condition at temperature range between 303 K and 573 K. The wavelength is 0.578375(1) Å.

Pressure-Composition Isotherms Measurement

PC isotherms were measured at hydrogen pressure range between 0 and ca. 100 kPa at 303 K by a volumetric technique using a pressure-composition-temperature apparatus (Suzuki Shokan Co., Ltd).

Solid-State ^2H NMR Spectra Measurement

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. Each sample was evacuated in a glass capillary for several hours at 373 K, and then each sample was sealed into a glass capillary with 86.7 kPa of ^2H gas at 303 K.

X-ray Photoelectron Spectroscopy Analysis

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.

2.3 Results and Discussion

TEM images of the synthesized $\text{Ag}_x\text{Rh}_{1-x}$ nanoparticles were recorded on a JEOL JEM-2000EX TEM instrument (Fig. 2.1). 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. The size distributions were narrow and the mean diameters were estimated by averaging over at least 300 particles.

The crystal structures of $\text{Ag}_x\text{Rh}_{1-x}$ bimetallic nanoparticles were investigated by synchrotron X-ray ($\lambda = 0.55277 \text{ \AA}$) powder diffraction at the beam line BL02B2, SPring-8. The diffraction patterns of the samples sealed in glass capillaries under vacuum were measured at 303 K. Figure 2.2 shows the XRD patterns of the Ag and Rh, and three compositions of AgRh nanoparticles ($\text{Ag}_{0.7}\text{Rh}_{0.3}$, $\text{Ag}_{0.5}\text{Rh}_{0.5}$ and $\text{Ag}_{0.4}\text{Rh}_{0.6}$). All the AgRh samples showed diffraction patterns consistent with single face-centered-cubic structure without signals from pure

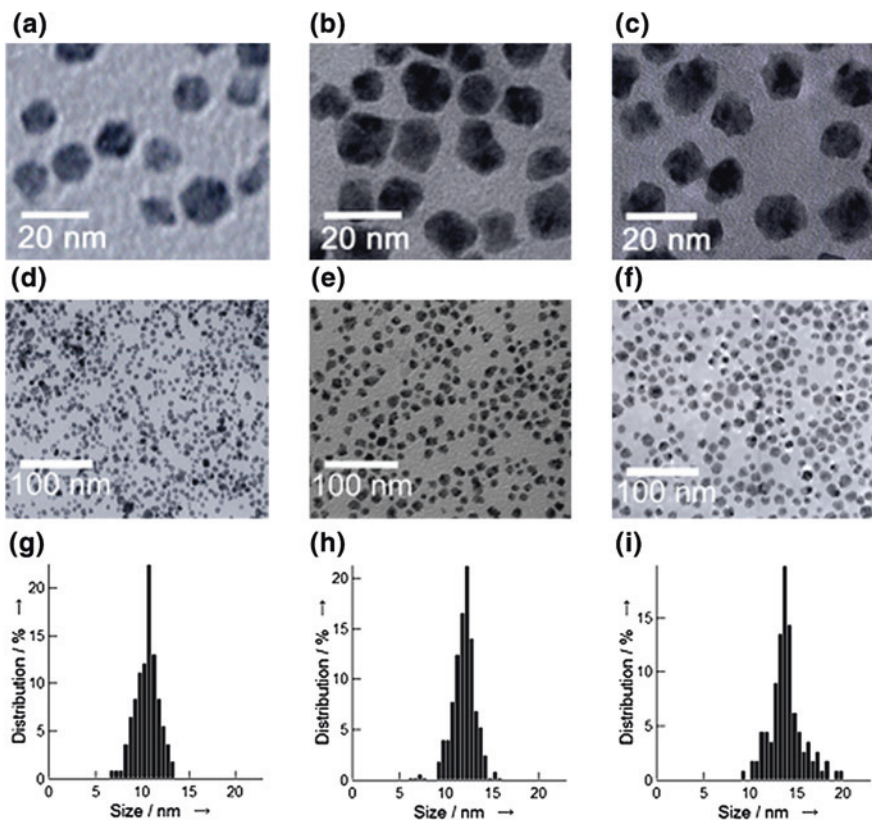


Fig. 2.1 The TEM images and the size distributions of **a, d, g** $\text{Ag}_{0.4}\text{Rh}_{0.6}$, **b, e, h** $\text{Ag}_{0.5}\text{Rh}_{0.5}$, and **c, f, i** $\text{Ag}_{0.7}\text{Rh}_{0.3}$

Ag or Rh phases (Fig. 2.2a). The diffraction peaks of AgRh nanoparticles shifted continuously to the higher-angle side with increasing Rh content in the AgRh nanoparticles, which is in agreement with the shrinkage of the lattice parameter due to the smaller unit cell parameter of Rh (Fig. 2.2b). This result strongly supports the formation of the atomic-level AgRh alloy.

To investigate the composition of Ag and Rh atoms in the nanoparticles, elemental analyses were carried out using AAS and EDX techniques (Table 2.1). The average stoichiometry from the AAS data was Ag:Rh = 0.51:0.49 and that from the EDX data was Ag:Rh = 0.49:0.51.

Figure 2.3 shows elemental mapping data for a group of prepared Ag_{0.5}Rh_{0.5} nanoparticles. Figure 2.3a shows a HAADF-STEM image. Figure 2.3b and c show the corresponding Ag–L and Rh–L STEM-EDX maps, respectively. Figure 2.3d presents an overlay map of the Ag and Rh chemical distribution. The mapping data (Fig. 2.3d) provides visually apparent evidence of the formation of AgRh solid solutions.

The author further characterized the AgRh nanoparticles by EDX line scanning analysis (Fig. 2.4). The line-scan position of the nanoparticle is denoted by the white line in the inset of Fig. 2.4. The compositional line profiles of Ag and Rh on a Ag_{0.5}Rh_{0.5} nanoparticle show that atomic-level Ag–Rh alloying successfully occurs (Fig. 2.5).

In order to investigate the change of the optical properties accompanied by the formation of AgRh solid solution, UV-Vis absorption spectra were measured with

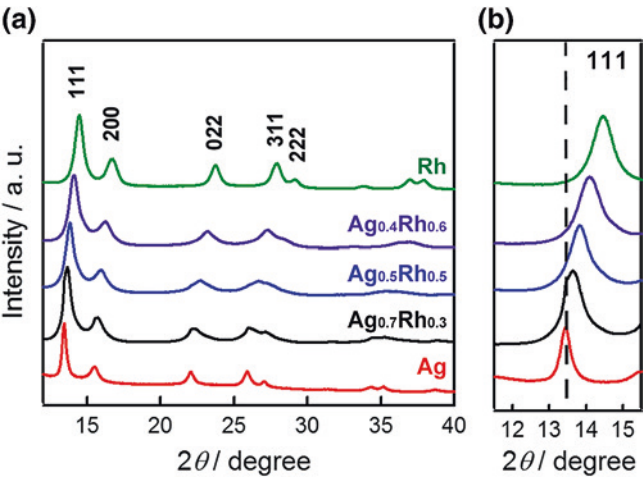


Fig. 2.2 a Synchrotron X-ray powder diffraction patterns ($2\theta = 12^{\circ}$ – 40°) of Ag, Rh, and Ag–Rh nanoparticles at 303 K, b ($2\theta = 11^{\circ}$ – 16°)

Table 2.1 Results of the particle composition of Ag–Rh bimetallic nanoparticles

AAS results	EDX results
Ag _{0.4} Rh _{0.6}	Ag _{0.38} Rh _{0.62}
Ag _{0.51} Rh _{0.49}	Ag _{0.49} Rh _{0.51}
Ag _{0.66} Rh _{0.34}	Ag _{0.69} Rh _{0.31}

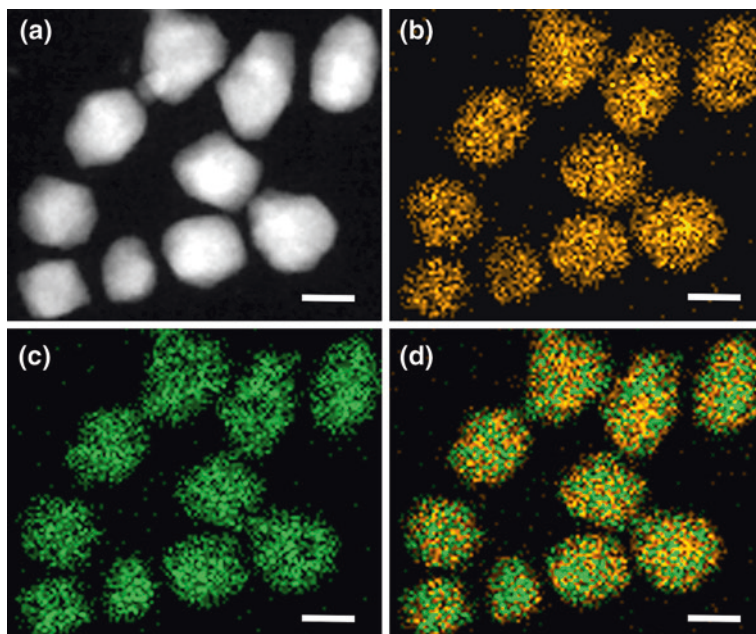


Fig. 2.3 The **a** HAADF-STEM image, **b** Ag-L STEM-EDX map and **c** Rh-L STEM-EDX map obtained from a group of prepared $\text{Ag}_{0.5}\text{Rh}_{0.5}$ nanoparticles. **d** The reconstructed overlay image of the maps shown in **b** and **c** (green Rh; orange Ag). The scale bars correspond to 10 nm (colour figure online)

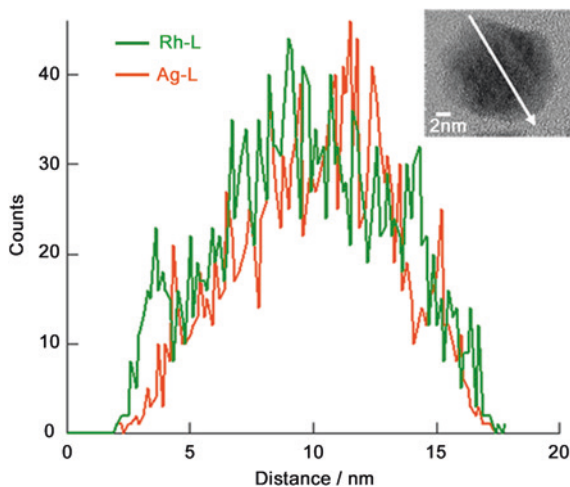


Fig. 2.4 Compositional line profiles of Ag and Rh from a $\text{Ag}_{0.5}\text{Rh}_{0.5}$ alloy nanoparticle recorded along the *arrow* shown in the STEM image (inset). Ag-L and Rh-L refer to the L electron shells of the Ag and Rh atoms, respectively. The profiles were obtained by plotting the integrated intensities at the Ag L-shell and Rh L-shell ionization edges

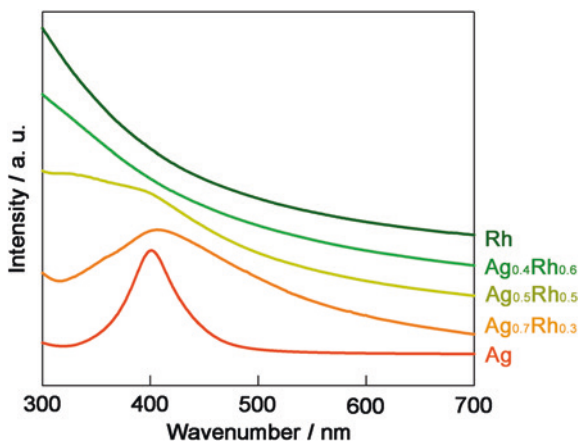


Fig. 2.5 UV-Vis absorption spectra of AgRh solid solution nanoparticles at various molar ratios

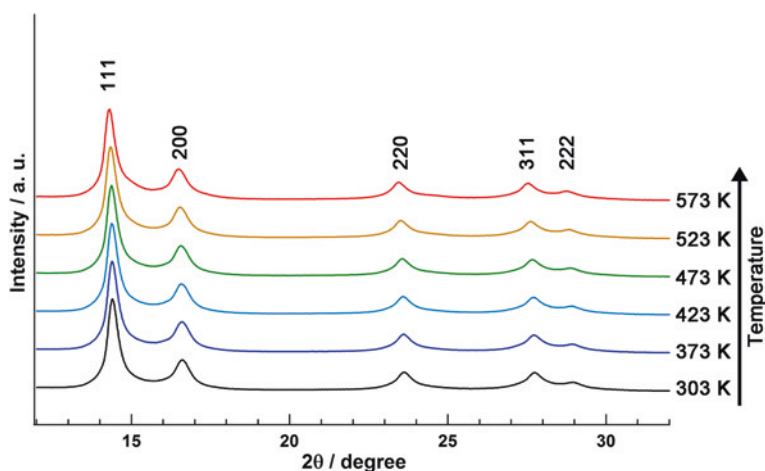


Fig. 2.6 The in situ XRD patterns of $\text{Ag}_{0.5}\text{Rh}_{0.5}$ nanoparticles measured under vacuum condition at temperature range between 303 and 573 K. The wavelength is 0.578375(1) Å

a Jasco V-570 spectrophotometer. The AgRh 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 AgRh 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 AgRh, indicating the formation of AgRh solid solution nanoparticles. To further investigate the thermal stability of $\text{Ag}_{0.5}\text{Rh}_{0.5}$ nanoparticles, in situ powder XRD measurements were performed at the beamline BL02B2, at SPring-8 (Fig. 2.6). It was found that the prepared $\text{Ag}_{0.5}\text{Rh}_{0.5}$ nanoparticles show the original structure up to 573 K.

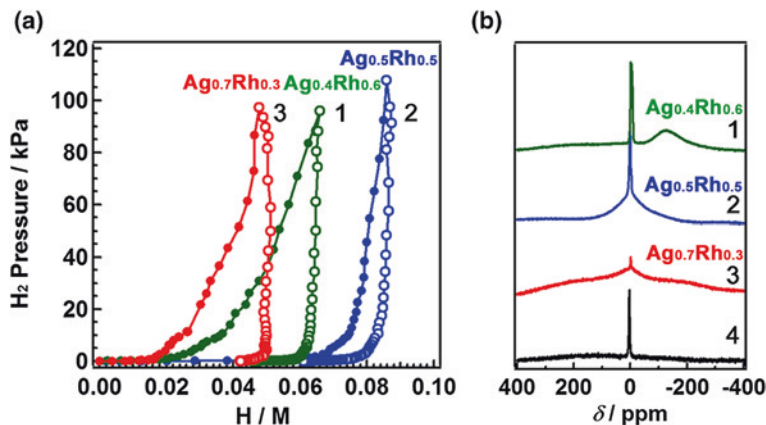


Fig. 2.7 **a** PC isotherms of (1) Ag_{0.4}Rh_{0.6}, (2) Ag_{0.5}Rh_{0.5}, and (3) Ag_{0.7}Rh_{0.3} nanoparticles (black circle absorption at 303 K; white circle desorption at 303 K). **b** Solid-state ²H NMR spectra for (1) Ag_{0.4}Rh_{0.6}, and (2) Ag_{0.5}Rh_{0.5}, (3) Ag_{0.7}Rh_{0.3} nanoparticles, and (4) ²H₂ gas. All the samples were measured under 86.7 kPa of ²H₂ gas at 303 K

To investigate the hydrogen storage properties of the AgRh nanoparticles, hydrogen pressure-composition isotherms were measured. Studies on hydrogen storage properties give important information related to the electronic state of metals [24–28]. As shown in Fig. 2.7a, the total amount of hydrogen absorption of Ag_{0.5}Rh_{0.5} nanoparticles was 0.09 H/M (M = Ag_{0.5}Rh_{0.5}) at ca. 100 kPa, whereas the absorptions of Ag_{0.7}Rh_{0.3} and Ag_{0.4}Rh_{0.6} nanoparticles were 0.05 H/M (M = Ag_{0.7}Rh_{0.3}) and 0.06 H/M (M = Ag_{0.4}Rh_{0.6}), respectively. The total amount of hydrogen absorption reached a maximum at the ratio of Ag:Rh = 50:50, where the electronic structure is expected to be similar to that of Pd. As seen in Fig. 2.7a, the amount of hydrogen absorption depends on the metal composition of the alloy. Accordingly, this difference in the amounts of hydrogen absorption implies a difference in the electronic structures of Ag_xRh_{1-x} nanoparticles.

Solid-state ²H NMR measurements were performed to investigate the state of ²H in the AgRh nanoparticles (Fig. 2.7b). In the spectrum of Ag_{0.5}Rh_{0.5} nanoparticles, a broad absorption line with a full width at half maximum of ca. 146 ppm at ca. -2.3 ppm and a sharp line around 0 ppm were observed. In the spectrum of ²H₂ gas (Fig. 2.7b–4), only a sharp line at 3.4 ppm was obtained. On comparison of these spectra, it is reasonable to attribute the sharp line in the spectrum of the Ag_{0.5}Rh_{0.5} particle to free deuterium gas (²H₂) and the broad component to absorbed deuterium atoms (²H) in the particles. The broad absorption lines of deuterium absorbed inside the lattices of Ag_{0.7}Rh_{0.3} and Ag_{0.4}Rh_{0.6} nanoparticles were observed at ca. 4.4 and -132.9 ppm, respectively (Fig. 2.7b–1, 3). These chemical shifts that give rise to the broad absorption lines suggest that the deuterium atoms inside the nanoparticles perceive the different potentials, and atomic-level alloying occurs in the Ag–Rh system.

The change in the electronic structure due to atomic-level alloying of Rh and Ag was investigated by XPS measurement (Fig. 2.8). The binding energies were

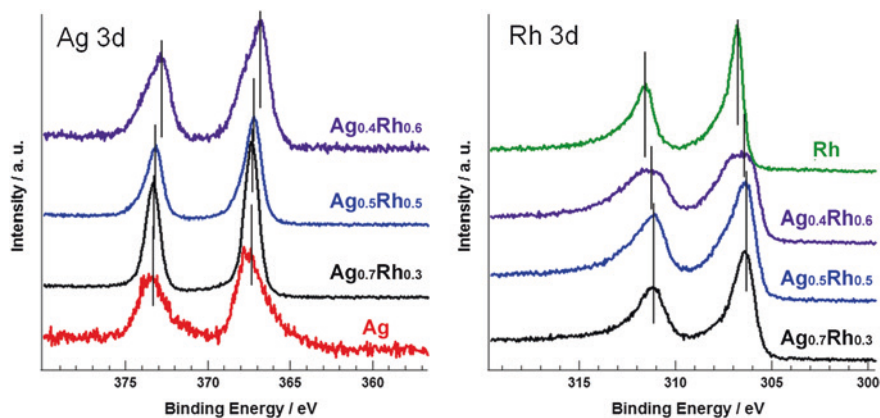


Fig. 2.8 The Ag 3d and Rh 3d core-level XPS of $\text{Ag}_x\text{Rh}_{1-x}$ nanoparticles

Table 2.2 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
$\text{Ag}_{0.4}\text{Rh}_{0.6}$	372.85	366.87	311.25	306.39
$\text{Ag}_{0.5}\text{Rh}_{0.5}$	373.16	367.17	311.14	306.35
$\text{Ag}_{0.7}\text{Rh}_{0.3}$	373.32	367.30	311.14	306.36
Ag	373.38	367.39		

corrected by reference to the C(1s) line at 284.5 eV. Figure 2.8 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 2.2. In Ag 3d, spectral shift is different from the general shifts [29]. If silver is oxidized, the binding energy is shifted to lower energy. In Fig. 2.8, Ag 3d binding energies of alloys shifted continuously to the lower energy with increasing Rh content, which is in agreement with the oxidation 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.

2.4 Conclusion

In summary, the author used the chemical reduction method to obtain, for the first time, solid solutions of PVP-protected AgRh alloys that are intimately mixed at the atomic level. The atomic-level Ag–Rh alloying was confirmed by means of EDX, and XRD measurements. It is known that Ag and Rh do not mix but form segregated clustering of each element, even in the liquid phase at around 2,000 °C [9]. Consequently, solid solution AgRh alloys cannot be obtained even by means

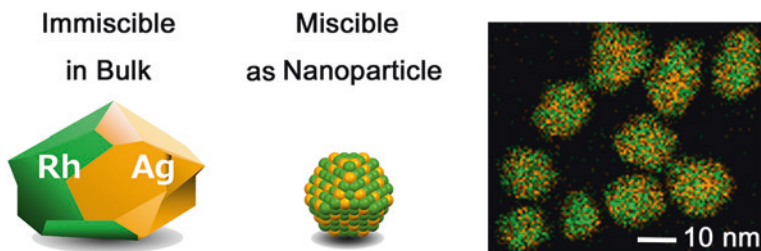


Fig. 2.9 Graphical abstraction of hydrogen storage properties of solid solution alloys of immiscible neighboring elements with Pd

of quenching techniques, and no knowledge of the structure or the electronic structure of the alloys was available. Our results contribute to the limited knowledge in this area. Furthermore, the prepared AgRh alloys show hydrogen storage properties; the $\text{Ag}_{0.5}\text{Rh}_{0.5}$ alloy exhibits the largest amount of hydrogen absorption in the alloys. However, the H/M value of $\text{Ag}_{0.5}\text{Rh}_{0.5}$ is about half amount of Pd nanoparticles. From our experimental results, it is conclude that the $\text{Ag}_{0.5}\text{Rh}_{0.5}$ solid solution alloy has a similar electronic structure to Pd, that is to say, “modern alchemy”. Following on from the discovery of the AgRh solid solution alloy, the author envisage the development of new solid solution alloys of immiscible Ag–Ni, Au–Rh, Cu–Ru, and other systems that exhibit phase-segregated structures even in high-temperature liquid phase [10, 30, 31] (Fig. 2.9).

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Hydrogen-Storage and Catalytic Properties

Kusada, K.

2014, XII, 78 p. 59 illus., 23 illus. in color., Hardcover

ISBN: 978-4-431-55086-0