

Spectroscopic study of hydrogen storage of Mg-Pd nanocomposite material

**Satoshi Ogawa¹, Taishi Fujimoto¹, Chie Tsukada¹, Masahiro Ogawa²,
Toshiaki Ohta², Tomoko Yoshida^{1,3}, Shinya Yagi^{1,3}**

1) Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, 464-8603, Japan

2) The SR center, Ritsumeikan University, 1-1-1 Noji-Higashi, Kusatsu, Shiga, 525-8577, Japan

3) EcoTopia Science Institute, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, 464-8603, Japan

Abstract

The hydrogen storage property of the composite of Mg and Pd nanoparticles (Mg NPs-Pd NPs) has been investigated by the QCM technique without the exposure to the air. The Mg NPs-Pd NPs can absorb the hydrogen under the room temperature and 760 Torr of H₂ gas. However, the desorption of the hydrogen has not been observed under the vacuum condition. We have also studied the chemical state of the Mg NPs-Pd NPs by XPS and XAFS. The XPS spectra have shown the interfacial Mg-Pd alloy state between the Mg NPs and Pd NPs. The XAFS analyses have revealed that the MgH₂ in the Mg NPs can not be dehydrogenated at the room temperature in spite of the high catalytic activity of Pd.

1. Introduction

Magnesium (Mg) is the most promising material for the application of hydrogen storage because of the high hydrogen storage capacity of MgH_2 up to 7.6 wt%. The problem of Mg for the practical application is energetic efficiency of the hydro-/dehydrogenation reactions. The both hydro-/dehydrogenation reactions of Mg require high temperature more than 350 °C and high pressure of hydrogen gas more than 3 MPa due to the low surface activity of Mg and the difficulty of the diffusion of hydrogen atoms through the MgH_2 layer [1, 2]. The surface activity of Mg is improved by the covering the Mg surface with the transition metals. The Mg thin film capped with palladium (Pd) can absorb and desorb the hydrogen gas under the room temperature [3]. It is noteworthy that the hydrogenation of the Mg layer has been completed within a few seconds due to the fast diffusion of hydrogen atoms from the Pd surface through the Mg-Pd alloy layer at the interface between the Pd and Mg phases. However, the diffusion of hydrogen inside of the bulk is inhibited by MgH_2 [1]. It is favorable for the further improvement of hydrogen diffusion kinetics that the size of Mg is decreased to nano-meter order e.g. nanoparticles (NPs). The NPs have the quite short diffusion length of hydrogen in comparison with the bulk.

In our previous work, the NPs composed of both Mg and Pd (Mg-Pd NPs) have been fabricated by the gas evaporation method using helium (He) gas [4, 5]. The sizes of the Mg-Pd NPs have distributed in the narrow range of 2-10 nm. The hydrogen storage property of the Mg-Pd NPs has been investigated by the quartz crystal microbalance (QCM) [5]. The Mg-Pd NPs have shown the hydrogen absorption under the room temperature up to 4.6 wt%. On the other hand, the desorption of hydrogen has not been observed in spite of the high vacuum condition. This irreversible behavior has seemed to be caused by the covering the surface of NPs with MgH_2 which inhibits the recombination of the hydrogen atoms on the surface.

In this study, we have investigated the hydrogen storage property and the chemical state of the composite of the Mg NPs and Pd NPs (Mg NPs-Pd NPs) by the QCM, X-ray photoelectron spectroscopy (XPS) and near Mg K-, Pd L₃-edges X-ray absorption fine structure analyses (Mg K- and Pd L₃-edges NEXAFS). The reversible hydrogen absorption and desorption can be expected for the Mg NPs-Pd NPs because the Pd NPs are separated from the Mg NPs initially i.e. the migration of the Mg toward the Pd surface is inhibited.

2. Experimental

Fabrication of the Mg NPs-Pd NPs

The Mg NPs-Pd NPs were fabricated by the gas evaporation method using He gas (purity: 99.99995 %). The gas evaporation method is suitable for the fabrication of NPs with clean surfaces i.e. absence of surfactants and contaminations. The rod shaped Mg and Pd wire were used as the evaporation sources. These sources were equipped in the individual evaporation chambers and were evaporated simultaneously under 80 Torr of He gas. The Mg and Pd NPs have been formed by aggregation of the evaporated Mg and Pd atoms under the He gas atmosphere, respectively. The Mg and Pd NPs were codeposited on the Ni polycrystalline substrate for the XPS and XAFS measurements. Fig. 2 shows the bright field image of the Mg and Pd NPs obtained by the transmission electron microscopy (TEM). The diameters of the Mg and Pd NPs distribute between 5-40 and 2-6 nm, respectively.

The Mg NPs-Pd NPs were also deposited on the quartz crystal capped with gold electrodes. The QCM has the high mass sensitivity less than a few nano-gram. The pressure-composition isotherm (P-C isotherm) for the hydrogen absorption of the Mg NPs-Pd NPs can be obtained by the exposure of the Mg NPs-Pd NPs to the pure hydrogen gas (99.99%) [5]. The two types of the Mg NPs-Pd NPs have been fabricated in this study. The one is the relatively Pd-rich Mg NPs-Pd NPs sample (Mg NPs-Pd NPs_1) and the other one is the relatively Mg-rich Mg NPs-Pd NPs sample (Mg NPs-Pd NPs_2). The nominal atomic ratio (Mg/Pd) of the each sample are 4 for Mg NPs-Pd NPs_1 and 10 for Mg NPs-Pd NPs_2.

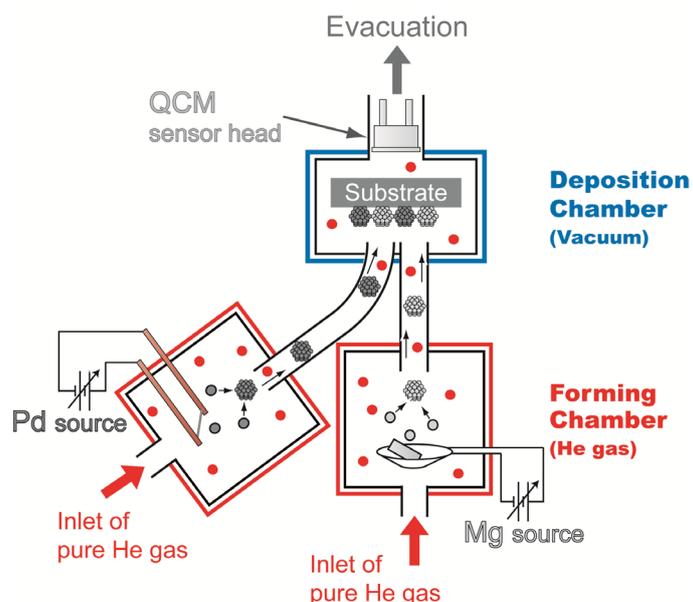


Fig. 1 Schematic view of the fabrication chamber of the Mg NPs-Pd NPs.

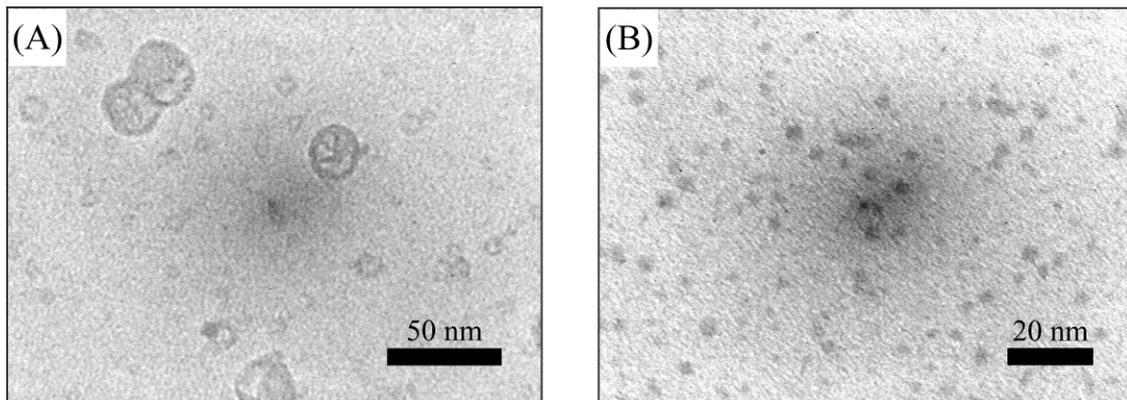


Fig. 2 TEM bright field image of the (A) Mg NPs and (B) Pd NPs.

XPS measurement

After the fabrication of the Mg NPs-Pd NPs, the fabrication chamber was evacuated to high vacuum of $\sim 1 \times 10^{-7}$ Torr. The Mg NPs-Pd NPs deposited on the Ni substrate were transferred to the ultra-high vacuum chamber ($\sim 5 \times 10^{-10}$ Torr) for the XPS measurement. The XPS measurements were performed using Mg K α X-ray (1253.6 eV) source and a hemispherical electron energy analyzer (PHOIBOS 100, SPECS GmbH). The XPS spectra were deconvoluted into each component by using CasaXPSTM software [6].

Mg K- and Pd L₃-edges NEXAFS measurement

Mg K- and Pd L₃-edges NEXAFS measurements were carried out at BL-10 of the SR center in Ritsumeikan University [7, 8]. A Golovchenko-type double-crystal monochromator with Beryl(10-10) for Mg K-edge and Ge(111) for Pd L₃-edge were used for the monochromatization of incident X-ray. The NEXAFS measurements were carried out using the total electron yield method by the sample drain current. In order to avoid the air oxidation of the Mg NPs-Pd NPs, the fabrication chamber of the Mg NPs-Pd NPs was connected to the XAFS chamber directly.

3. Results and Discussion

3.1 Surface chemical analysis by XPS

Fig. 3 shows the Pd3d_{5/2} XPS spectra of the as-prepared Mg NPs-Pd NPs. The both peak tops in Fig. 3 shift toward higher binding energy side compared with that of the metallic state (Pd⁰ at 335.5 eV). The both spectra can be deconvoluted into the two chemical states with the pseudo Voigt functions. The one of the chemical states is the metallic Pd (Pd⁰). The other one is located around 336 eV which does not correspond to the peak position of PdO (337.0 eV). It is reasonable to attribute this chemical state to the Mg-Pd alloy (intermetallic

compound). The chemical shift to the higher binding energy side compared with metallic state represents that the charge transfer to the Mg atom from the Pd atom. Fig.3 shows clearly that the Mg NPs-Pd NPs 2 possess the more Mg-Pd alloy phase than the Mg NPs-Pd NPs 1. The Mg-Pd alloy phase is formed at interface between the Mg and Pd NPs. The difference of the amount of the Mg-Pd alloy is reflected the difference of the interfacial area between Mg NPs-Pd NPs 1 and Mg NPs-Pd NPs 2.

3.2 Hydrogen absorption and desorption properties of the Mg NPs-Pd NPs

The P-C isotherms of the Mg NPs-Pd NPs samples are shown in Fig. 4. The both P-C isotherms have the two plateau regions. The 1st plateau at ~ 0.3 Torr is attributed to the hydrogenation of the Mg phase [9] and the 2nd plateau region at ~ 30 Torr is attributed to the hydrogenation of the Pd phase. The 2nd plateau is located higher than that of the pure Pd (~ 15 Torr) due to the interfacial alloying with Mg [10].

The hydrogen storage absorption of the Mg NPs-Pd NPs 1 and 2 reach to 2.0 and 3.9 wt% at the 303 K under the 760 Torr of H_2 , respectively. The both Mg NPs-Pd NPs samples can absorb the hydrogen under the much lower temperature and pressure of hydrogen in comparison with the previous study [11] because of the absence of the air oxidation products on the surface. The hydrogen storage capacities of the Mg NPs-Pd NPs samples are much lower than the ideal storage capacities which are estimated by the atomic ratio of Mg and Pd (3.9 wt% for Mg NPs-Pd NPs 1 and 6.8 wt% for Mg NPs-Pd NPs 2). These results imply the residual metallic Mg in the Mg NPs. Moreover, the dehydrogenations of the Mg NPs-Pd NPs have not been observed as shown in Fig. 4. This represents that the 1st

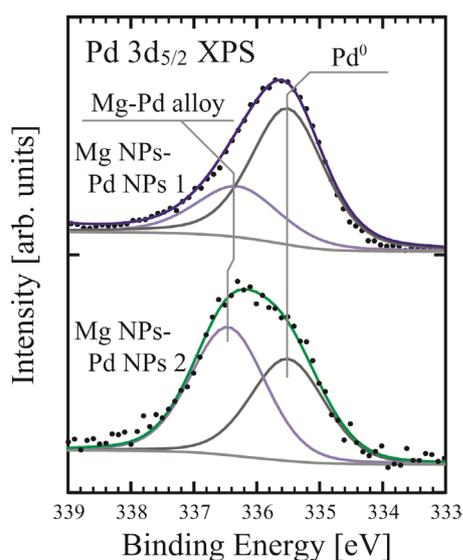


Fig. 3 XPS spectra for the Pd $3d_{5/2}$ core electrons of the Mg NPs-Pd NPs.

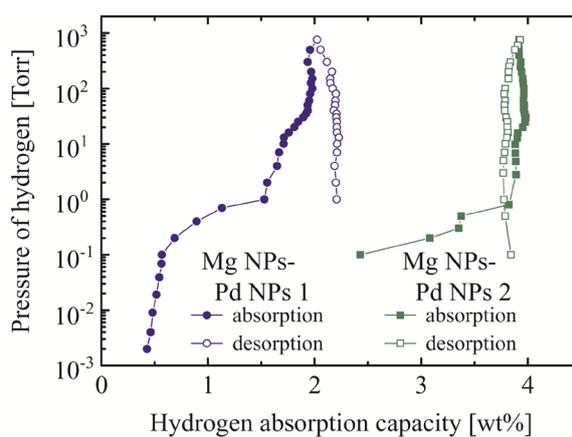


Fig. 4 P-C isotherm of the Mg NPs-Pd NPs obtained at 30 °C. These P-C isotherms were measured without the exposure of the samples to the air.

hydrogenation reactions of the Mg NPs-Pd NPs are irreversible, in other words the hydrogen atoms are stabilized at the Mg or Pd phases.

3.3 Mg K- and Pd L₃-edges NEXAFS analyses of the Mg NPs-Pd NPs

Fig. 5 shows the Mg K- and Pd L₃-edges NEXAFS spectra of the Mg NPs-Pd NPs before and after hydrogenation. The NEXAFS spectra for the metallic state of the each absorption atom are shown as the reference spectra.

In the Mg K-edge NEXAFS spectra, the shoulder structure around 1304 eV is the specific feature of the metallic Mg state. This structure can be seen in the NEXAFS spectrum of the Mg NPs-Pd NPs before the exposure to the hydrogen and the shape of the NEXAFS spectrum is quite similar to that of the Mg bulk. This represents that the most of the Mg atoms in the Mg NPs-Pd NPs have no interaction with the other elements e.g. oxygen or Pd. It seems that the Mg-Pd alloy phase between the Mg NPs and Pd NPs is obscured due to the bulk sensitivity of XAFS in comparison with XPS.

The shape of the NEXAFS spectrum changes dramatically after the exposure to the hydrogen. The intensity of the shoulder structure decreases and new peak structure is seen around 1307 eV. This peak is specific feature of the NEXAFS for MgH₂ [12]. Although the NEXAFS measurement has been carried out under the high vacuum, the MgH₂ has not been dehydrogenated. This behavior corresponds with that of the P-C isotherm in Fig. 4. Moreover, the shoulder structure in the spectrum for the Mg NPs-Pd NPs after hydrogenation indicates the residual metallic Mg in the Mg NPs, which is also consistent with the result of the P-C isotherm.

The Pd L₃-edge NEXAFS spectra in Fig. 5 show that the chemical state of the Pd has not changed dramatically before and after the exposure to the hydrogen. The shape of the NEXAFS spectrum of the Mg NPs-Pd NPs is similar entirely to that of the Pd bulk. After the exposure to the hydrogen, the peak position shifts slightly to the high energy side. This shift cannot be simulated by the linear combination fitting with the spectra for the metallic and hydrogenated Pd phases. It is attributed to the increase of the fraction of the Mg-Pd alloy at the interface between the Mg NPs and the Pd NPs. This change of the chemical state cannot be the factor for the inhibition of the dehydrogenation of MgH₂ because the Mg-Pd alloy improves the hydrogen diffusion between Mg and Pd.

The results in Fig. 5 suggest that the dehydrogenation of the Mg NPs is limited by the thermal stability of the MgH₂. In the case of the Mg-Pd NPs, the remaining PdH_x after the evacuation of the hydrogen indicates that the dehydrogenation of the Mg is inhibited by the covering of the Pd phase with the MgH₂ [5]. This effect is excluded in this study because hydrogenated Pd has not been observed in Fig. 5. It seems that the Mg NPs require the more

interface with the Pd for the dehydrogenation of MgH_2 because the Mg thin film capped with the Pd shows the reversible hydro-/dehydrogenation at the room temperature. Otherwise, the further size-down of the Mg or the alloying with the transition metals are effective for the improvement of the dehydrogenation of the MgH_2 .

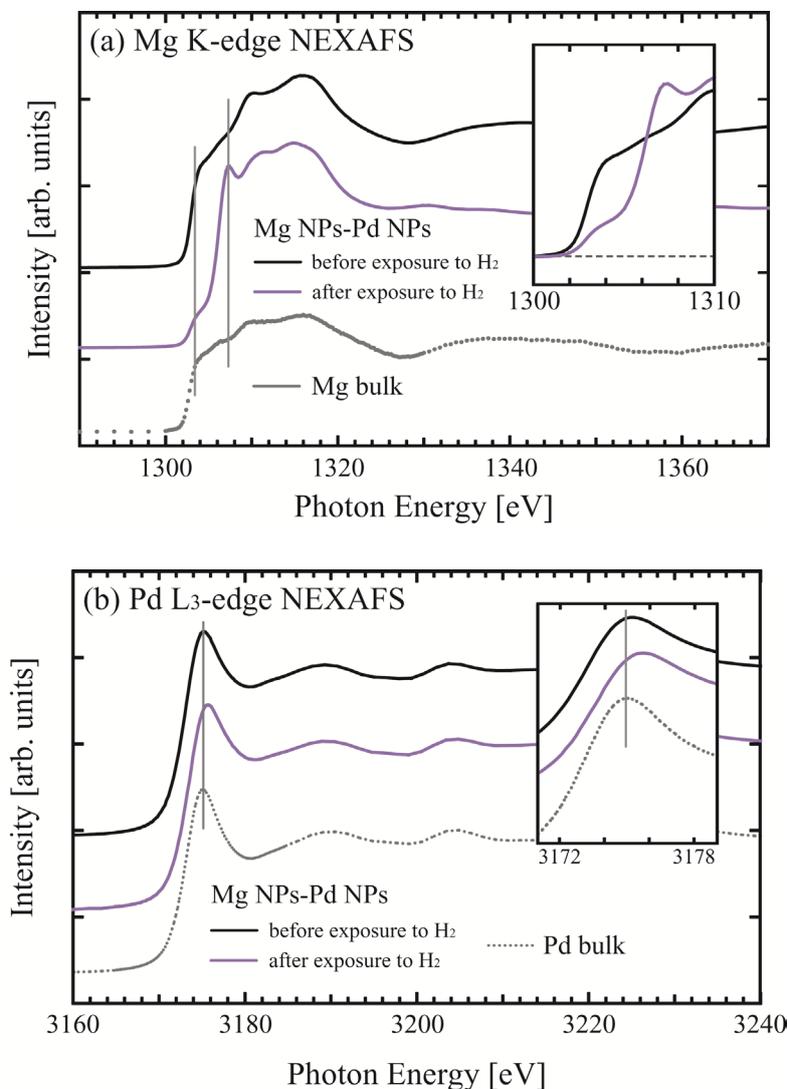


Fig. 5 (a) Mg K- and (b) Pd L₃-edges NEXAFS spectra of the Mg NPs-Pd NPs.

4. Conclusions

The Mg NPs-Pd NPs with the clean surfaces have been fabricated by the gas evaporation method using He gas. The hydrogen storage properties and the chemical state of the Mg NPs-Pd NPs have been investigated by the QCM, XPS and NEXAFS without the air oxidation. The Mg NPs-Pd NPs samples can absorb the hydrogen under the room temperature and 760 Torr of H₂; however, the desorption of the hydrogen have not been observed. The Mg K- and Pd L₃-edges NEXAFS analyses for the Mg NPs-Pd NPs have

revealed that the MgH₂ in the Mg NPs can not be dehydrogenated in spite of the coexistence of the Pd NPs. It seems that the catalytic effect of the Pd NPs has not been sufficient for the dehydrogenation of MgH₂.

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