Atomic-Level Pd-Au Alloying and Controllable Hydrogen-Absorption Properties in Size-Controlled Nanoparticles Synthesized by Hydrogen Reduction Method†

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Size-controlled atomic-level Pd-Au alloy nanoparticles have been synthesized with a wide range of atomic raios by a facile method
10 **using H₂ gas, and their controllable hydrogen-absorption properties have been studied from hydrogen pressure-composition isotherms and solid-state ²H NMR spectra.**

Bimetallic nanoparticles have attracted great interest as magnetic,[1] optical[2] and catalytic materials[3] in many fields of 15 science and technology due to their unique and different properties from those of the monometallic nanoparticles. Pd-Au bimetallic nanoparticles are the significant systems, and they play an important role as the effective catalysts in the direct synthesis of hydrogen peroxide from H₂ and O₂, the 20 hydrodesulfurization of thiophene, the oxidation of alcohols to aldehydes, etc. The enhanced performance can directly be attributed to the synergistic effects of Pd-Au alloying. Due to the wide applications of these Pd-Au catalysts, it is of great interest to study the structure of the bimetallic nanoparticles. 25 Various phase-separated structures such as core/shell[4] or cluster-in-cluster,[5] or alloy structures[6] have been reported. On the other hand, a few reports are there on the solid-solution structured alloy nanoparticles[7] where Pd and Au are homogeneously mixed at the atomic level. Most of the Pd-Au 30 nanoparticles reported were supported on carbon, activated carbon, or Al₂O₃.[7a-e] A limited number of the reports regarding on the solid-solution nanoparticles originates from the fact that Pd and Au are hard to mix at the atomic level due to their segregation tendency.[8] The further development of a 35 facile and effective synthesis method for the size-controllable solid-solution Pd-Au nanopartcles is, therefore, still required for technical applications with high efficiency and performance.

In this study, we have synthesized size-contorolled solid-40 solution alloy nanoparticles where Pd and Au are homogeneously mixed at the atomic level with a wide range of atomic ratios by the successive method using H₂ gas as a reducing agent (Fig. 1). A detailed investigation of the structure of the Pd-Au nanoparticles was carried out using 45 high-resolution transmission electron microscopy (HRTEM), energy dispersive spectra (EDS) and powder X-ray diffractions (XRD). Moreover, we have studied the hydrogen-absorption properties of the Pd-Au nanoparticles from hydrogen pressure-composition (PC) isotherms and solid-state 50 ²H NMR spectra.

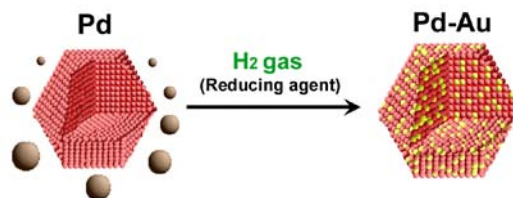Poly(*N*-vinyl-2-pyrrolidone) (PVP)-protected Pd

Fig. 1 Schematic view of as-made Pd-Au solid-solution nanoparticles during the successive reduction. (brown ; Au³⁺, red ; Pd, yellow ; Au)

nanoparticles were prepared from the alcoholic reduction of 55 palladium chloride (PdCl₂) in presence of PVP.[9] The aqueous solution of tetrachloroauric acid (HAuCl₄) was added to the thus-obtained Pd nanoparticles, with a diameter of 7.1 nm, and the mixture was vigorously stirred under H₂ gas. The atomic ratio of Pd and Au depends on the HAuCl₄ 60 concentration.

The atomic ratios of Pd and Au were determined by ICP-MS spectrometry, and the corresponding particles were characterized, Pd₈₀-Au₂₀, Pd₅₀-Au₅₀ and Pd₂₀-Au₈₀. From the results of TEM measurements (Fig. S1 in ESI†), the 65 corresponding mean diameters of the nanoparticles were 8.4 ± 1.6, 9.1 ± 1.7 and 10.1 ± 2.3 nm, respectively, and the size increased with the additional Au content. From the intensity and position of the surface plasmon resonance peak observed in the ultraviolet-visible absorption spectra for various Pd-Au 70 nanoparticles (Fig. S2 in ESI†), we confirmed the incorporation of Au atoms into Pd nanoparticles. All the Pd-Au nanoparticles showed the XRD patterns from a single face-centered-cubic (fcc) lattice (Figs S3a, S3b in ESI†). The diffraction peaks of Pd-Au nanoparticles shifted linearly to 75 the lower-angle side with increasing Au content in the Pd-Au nanoparticles in agreement with the larger unit cell parameter for Au (Fig. S3c in ESI†). These results strongly support the formation of the atomic-level Pd-Au alloy over the whole inside the particle.

80 In order to investigate the distribution of Pd and Au atoms inside the nanoparticle, HRTEM images and EDS spectra were measured for the Pd₈₀-Au₂₀ and Pd₅₀-Au₅₀ nanoparticles, as shown Figs 2a, 2c and Figs 2b, 2d, respectively. In general, each domain (phase separation) structure of Pd and Au such as 85 a core/shell type is observable in the HRTEM image due to the difference in contrast between Pd and Au atoms.[4a-d] The difference of such a contrast is not seen in Figs 2a and 2b,
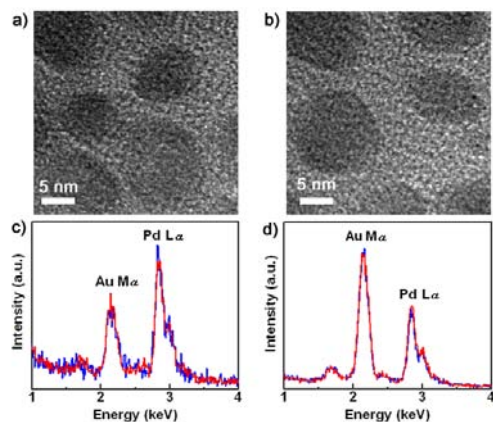
Fig. 2 HRTEM images and EDS spectra in (a) Pd_{80}-Au_{20} and (b) Pd_{50}-Au_{50} nanoparticles. The analysis was performed for the surface part (blue line) and center part (red line) with a 1nm electron beam.
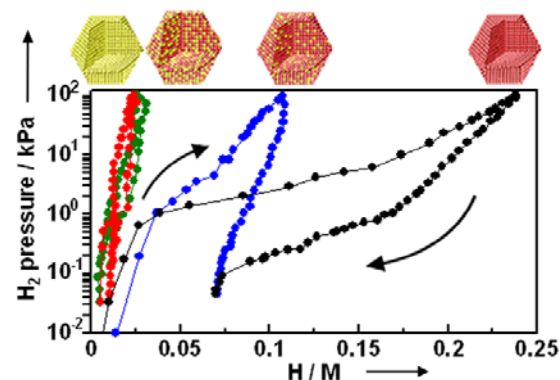
indicating that the structure of the obtained Pd-Au
5 nanoparticles is not phase-separated structure of Pd and Au. In the EDS spectrum for the Pd_{80}-Au_{20} nanoparticle (Fig. 2c), the X-ray emission lines from both Pd Lα and Au Mα were observed inside one nanoparticle, the difference between the intensity ratios of Pd Lα / Au Mα in the surface and the center
10 parts was not observed. From these results, it was revealed out that the obtained Pd-Au nanoparticles form a homogeneous solid solution alloy, where Pd and Au are mixing at the atomic level. The EDS spectrum for Pd_{50}-Au_{50} nanoparticles also showed the similar result to the Pd_{80}-Au_{20} nanoparticle; Pd
15 and Au atoms are homogeneously distributed in the nanoparticle (Fig. 2d). The atomic ratios of Pd and Au for Pd_{80}-Au_{20} and Pd_{50}-Au_{50} nanoparticles were estimated by the EDS spectra to be 86 : 14 and 50 : 50, respectively, and are consistent with the molar ratios determined by ICP-MAS.
20 Similarly, the distributions of Pd and Pt have been investigated for several particles and showed the same results that the intensity ratios of Pd Lα / Au Mα were equal. These results indicate the occurrence of Pd-Au alloying at the atomic level. It is well known that H atoms are generated on the
25 surface of Pd metal from H_2 gas and the H atoms are very active (the so-called nascent hydrogen) and therefore have high reducing ability. The formation of Pd-Au alloy is considered to originate not from the replacement between Pd and Au^{3+} but from the hydrogen reduction.[10]
30 It is also well known that hydrogen molecules can easily invade inside metal or alloy lattices as hydrogen atoms, and generate the defect structures with superabundant vacancies, leading to the atomic rearrangements of alloys.[11] The formation of the Pd-Au atomic-level alloy can be explained as
35 follows. First, Au^{3+} is reduced near the Pd surface by hydrogen, and the Au atoms diffuse into the inside of Pd nanoparticles owing to hydrogen-induced vacancies or lattice defects over the entire structure. Consequently, Pd and Au are mixing at the atomic level. Hydrogen gas is considered to
40 work as a double reagent to reduce Au^{3+} ions to Au atom and form vacancies, resulting in Pd-Au atomic level alloys.

Studies of hydrogen-absorption properties of the nanoparticles give important information related to the structure and the electronic state.[12] In order to investigate the

45 **Fig. 3** PC isotherms of Pd (black), Pd_{80}-Au_{20} (blue), Pd_{50}-Au_{50} (green) and Au nanoparticles (red). Isotherms were measured according direction of arrows. H/M shows the number of hydrogen atoms divided by the total number of metal.

change of the hydrogen-absorption properties accompanied by
50 the addition of Au atoms to Pd nanoparticles, PC isotherms of Pd-Au nanoparticles were measured at 303 K. As shown in Fig. 3, only 20 at% replacement of Pd with Au atom results in a reduction of more than half of total amount of hydrogen absorption. With the further addition of Au atoms, the Pd_{50}-
55 Au_{50} nanoparticles hardly absorbed hydrogen. It may be expected that the hydrogen concentration in the Pd_{50}-Au_{50} nanoparticles is equal to half that of Pd since Au nanoparticles does not absorb hydrogen. This drastic reduction of hydrogen absorption also indicates that the Pd-Au nanoparticles are not
60 exhibit phase-separation structure but is solid-solution type, where Pd and Au atoms are homogeneously mixed at the atomic level. In the desorption process of Pd and Pd_{80}-Au_{20} nanoparticles, the curve does not completely return back to the starting point, indicating that some hydrogen atoms are
65 strongly trapped inside the nanoparticles.[12a]

It is well known that the hydrogen concentration in Pd bulk is linked to the number of holes in the 4d conduction band.[13] As the 4d conduction band is filled, the hydrogen concentration is reduced. The band-filling effect on hydrogen
70 absorption has been reported in the cases of Pd-Ag[13a, 14] and Pd-Au[15] bulk alloys. In our experimental results, the decrease of the hydrogen concentrations originates from the filling up
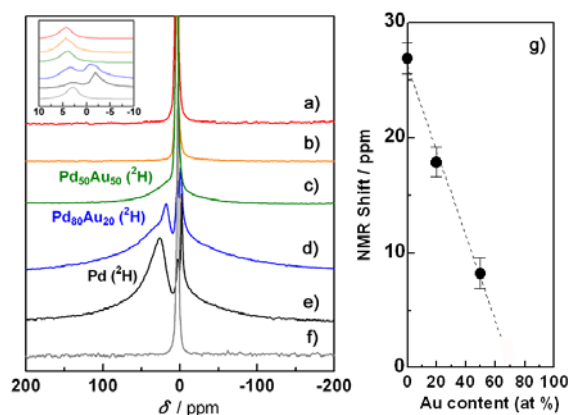

Fig. 4 Solid-state ^2H NMR spectra for the samples of Pd-Au nanoparticles at Pd/Au ratios = (d) 80/20, (c) 50/50, (b) 20/80. The samples of (f) $^2H_2$
75 gas, (e) Pd and (a) Au nanoparticles were also measured. (g). NMR shift of ^2H absorbed inside Pd-Au nanoparticles.

of the Pd 4d conduction band due to the addition of Au; 6s-electron of Au donates to the 4d-band of Pd and the numbers of 4d band holes in Pd-Au nanoparticles are decreased. (Fig. S4 in ESI†)

Solid-state ^{2}H NMR measurements were performed to investigate the states of ^{2}H in Pd-Au nanoparticles (Fig. 4b-d). The sharp line at around 0 ppm and broad absorption lines at a lower field were observed for Pd and Pd-Au nanoparticles with Au contents of 20 and 50 at% (Fig. 4c-e)). In the spectrum for ^{2}H$_2$ gas, only a sharp line at 3.4 ppm was observed. By comparison of these spectra, it is reasonable to attribute the sharp component in the spectrum of particle to free deuterium gas (^{2}H$_2$) and the broad component to absorbed deuterium atoms (^{2}H) (Fig. 4 inset). Additionally, in the spectra for samples of Pd and Pd$_{80}$-Au$_{20}$ nanoparticles, sharp components were observed at upper field in comparison with the peak position of free ^{2}H$_2$ gas, attributing to deuterium atoms diffusing and/or exchanging with free deuterium on the particles surface (Fig. 4 inset). It should be noted that the broad absorption lines, originating from ^{2}H inside the Pd-Au lattice, is markedly shifted to upfield linearly with the Au content (Fig. 4g). This shift implies an increase of the electron density around ^{2}H nuclei, which is caused by change in the occupancies of valence electrons due to hybridization of the valence bands.[16] This linear shift also demonstrates that atomic-level alloying occurs in Pd-Au system and deuterium in the nanoparticles perceives the different potentials depending on the composition of Pd and Au. Deuterium NMR is, therefore, very sensitive and a powerful probe to the electronic state of nanoparticles.

In summary, we have synthesized and characterized size-controlled alloy nanoparticles where Pd and Au are homogeneously mixed at the atomic level with a wide range of ratios by the successive reduction method using H$_2$ gas. The atomic-level Pd-Au alloying has been confirmed by means of HRTEM, EDS and XRD measurements. Only 20 at% of Au in Pd is sufficient to suppress the hydrogen absorption completely. The amount of hydrogen absorption is controllable at low-concentration alloying with Au and is considered to depend on the band filling of Pd 4d, which is consistent with the observed linear upfield shift of ^{2}H NMR signal. The atomic-level alloy of variable-size and size-controlled Pd-Au nanoparticles are expected to be useful as effective catalysts for various reactions. The present hydrogen reduction method gives us a big advantage for constructing various size-controlled Pd-Au nanoparticles by changing the size of Pd seeds.

Notes and references

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