Atomic-level Pd-Au alloying and controllable hydrogen-absorption properties in size-controlled nanoparticles synthesized by hydrogen reduction

Kobayashi, Hirokazu; Yamauchi, Miho; Ikeda, Ryuichi; Kitagawa, Hiroshi


2009

http://hdl.handle.net/2433/87373

c Royal Society of Chemistry 2009.; This is not the published version. Please cite only the published version.; この論文は出版社版でありません。引用の際には出版社版をご確認ご利用ください。
Atomic-Level Pd-Au Alloying and Controllable Hydrogen-Absorption Properties in Size-Controlled Nanoparticles Synthesized by Hydrogen Reduction Method†

Hirokazu Kobayashi, ‡a Miho Yamauchi§ab and Hiroshi Kitagawa¶*,a,c

Size-controlled atomic-level Pd-Au alloy nanoparticles have been synthesized with a wide range of atomic ratios by a facile method 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 optical2 and catalytic materials3 in many fields of 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 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.

Various phase-separated structures such as core/shell4 or cluster-in-cluster,5 or alloy structures6 have been reported. On the other hand, a few reports are there on the solid-solution structured alloy nanoparticles7 where Pd and Au are homogeneously mixed at the atomic level. Most of the Pd-Au nanoparticles reported were supported on carbon, activated carbon, or Al2O3.7a-e A limited number of the reports corresponding mean diameters of the nanoparticles were 8.4 ± 6.6, 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 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 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.

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 a core/shell type is observable in the HRTEM image due to the difference in contrast between Pd and Au atoms.7a-d The difference of such a contrast is not seen in Figs 2a and 2b.
indicating that the structure of the obtained Pd-Au 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 L$_{\alpha}$ and Au M$_{\alpha}$ were observed inside one nanoparticle, the difference between the intensity ratios of Pd L$_{\alpha}$ / Au M$_{\alpha}$ in the surface and the center 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 spectra for Pd$_{80}$-Au$_{20}$ nanoparticles also showed the similar result to the Pd$_{80}$-Au$_{20}$ nanoparticle; Pd 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.

Similarly, the distributions of Pd and Pt have been investigated for several particles and showed the same results that the intensity ratios of Pd L$_{\alpha}$ / Au M$_{\alpha}$ 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 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.

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. The formation of the Pd-Au atomic-level alloy can be explained as 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 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. In order to investigate the change of the hydrogen-absorption properties accompanied by 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$_{50}$-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 of that of Pd since Au nanoparticles do not absorb hydrogen. This drastic reduction of hydrogen absorption also indicates that the Pd-Au nanoparticles are not 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 strongly trapped inside the nanoparticles.

It is well known that the hydrogen concentration in Pd bulk is linked to the number of holes in the 4d conduction band. As the 4d conduction band is filled, the hydrogen concentration is reduced. The band-filling effect on hydrogen absorption has been reported in the cases of Pd-Ag and Pd-Au bulk alloys. In our experimental results, the decrease of the hydrogen concentrations originates from the filling up of the 4d conduction band.
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 ²H NMR measurements were performed to investigate the states of ²H 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 ²H₂ 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 (²H₂) and the broad component to adsorbed deuterium atoms (²H) (Fig. 4 inset). Additionally, in the spectra for samples of Pd and Pd₈₀-Au₂₀ nanoparticles, sharp components were observed at upper field in comparison with the peak position of free ²H₂ 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 ²H inside the Pd-Au lattice, is markedly shifted to upper field in comparison with the Au content (Fig. 4g). This shift implies an increase of the electron density around ²H nuclei, which is caused by change in the occupancies of valence electrons due to hybridization of the valence bands. This linear shift also demonstrates that atomic-level alloying occurs in Pd-Au system and 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 H₂ 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 ²H 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**

1. Department of Chemistry, Faculty of Science, Kyushu University, Hakoizaki 6-10-1, Fukuoka 812-8581, Japan E-mail: kitagawa@kuchem.kyoto-u.ac.jp; Fax: +75-753-4035; Tel: +75-753-4035
2. JST PRESTO, Sanbancho 5, Chiyoda-ku, Tokyo 102-0075, Japan
3. JST CREST, Sanbancho 5, Chiyoda-ku, Tokyo 102-0075, Japan
4. Current address: Department of Biomedical Engineering, Washington University, St. Louis, Missouri 63130, USA
5. Current address: Catalysis Research Center, Hokkaido University, West 10, North 21, Kita-ku, Sapporo 001-0021, Japan
6. Current address: Department of Chemistry, Graduate School of Science, Kyoto University, Kitashirakawa-Oiwakecho, Sakyo-ku, Kyoto 606-8502, Japan
7. Current address: Department of Chemistry, Graduate School of Science, Kyoto University, Kitashirakawa-Oiwakecho, Sakyo-ku, Kyoto 606-8502, Japan
8. Current address: Department of Chemistry, Graduate School of Science, Kyoto University, Kitashirakawa-Oiwakecho, Sakyo-ku, Kyoto 606-8502, Japan
9. Current address: Department of Chemistry, Graduate School of Science, Kyoto University, Kitashirakawa-Oiwakecho, Sakyo-ku, Kyoto 606-8502, Japan
10. Current address: Department of Chemistry, Graduate School of Science, Kyoto University, Kitashirakawa-Oiwakecho, Sakyo-ku, Kyoto 606-8502, Japan
11. Current address: Department of Chemistry, Graduate School of Science, Kyoto University, Kitashirakawa-Oiwakecho, Sakyo-ku, Kyoto 606-8502, Japan
12. Current address: Department of Chemistry, Graduate School of Science, Kyoto University, Kitashirakawa-Oiwakecho, Sakyo-ku, Kyoto 606-8502, Japan
13. Current address: Department of Chemistry, Graduate School of Science, Kyoto University, Kitashirakawa-Oiwakecho, Sakyo-ku, Kyoto 606-8502, Japan
14. Current address: Department of Chemistry, Graduate School of Science, Kyoto University, Kitashirakawa-Oiwakecho, Sakyo-ku, Kyoto 606-8502, Japan
15. Current address: Department of Chemistry, Graduate School of Science, Kyoto University, Kitashirakawa-Oiwakecho, Sakyo-ku, Kyoto 606-8502, Japan
16. Current address: Department of Chemistry, Graduate School of Science, Kyoto University, Kitashirakawa-Oiwakecho, Sakyo-ku, Kyoto 606-8502, Japan
17. Current address: Department of Chemistry, Graduate School of Science, Kyoto University, Kitashirakawa-Oiwakecho, Sakyo-ku, Kyoto 606-8502, Japan
18. Current address: Department of Chemistry, Graduate School of Science, Kyoto University, Kitashirakawa-Oiwakecho, Sakyo-ku, Kyoto 606-8502, Japan
19. Current address: Department of Chemistry, Graduate School of Science, Kyoto University, Kitashirakawa-Oiwakecho, Sakyo-ku, Kyoto 606-8502, Japan
20. Current address: Department of Chemistry, Graduate School of Science, Kyoto University, Kitashirakawa-Oiwakecho, Sakyo-ku, Kyoto 606-8502, Japan
21. Current address: Department of Chemistry, Graduate School of Science, Kyoto University, Kitashirakawa-Oiwakecho, Sakyo-ku, Kyoto 606-8502, Japan
22. Current address: Department of Chemistry, Graduate School of Science, Kyoto University, Kitashirakawa-Oiwakecho, Sakyo-ku, Kyoto 606-8502, Japan
23. Current address: Department of Chemistry, Graduate School of Science, Kyoto University, Kitashirakawa-Oiwakecho, Sakyo-ku, Kyoto 606-8502, Japan
24. Current address: Department of Chemistry, Graduate School of Science, Kyoto University, Kitashirakawa-Oiwakecho, Sakyo-ku, Kyoto 606-8502, Japan
25. Current address: Department of Chemistry, Graduate School of Science, Kyoto University, Kitashirakawa-Oiwakecho, Sakyo-ku, Kyoto 606-8502, Japan
26. Current address: Department of Chemistry, Graduate School of Science, Kyoto University, Kitashirakawa-Oiwakecho, Sakyo-ku, Kyoto 606-8502, Japan
27. Current address: Department of Chemistry, Graduate School of Science, Kyoto University, Kitashirakawa-Oiwakecho, Sakyo-ku, Kyoto 606-8502, Japan
28. Current address: Department of Chemistry, Graduate School of Science, Kyoto University, Kitashirakawa-Oiwakecho, Sakyo-ku, Kyoto 606-8502, Japan
29. Current address: Department of Chemistry, Graduate School of Science, Kyoto University, Kitashirakawa-Oiwakecho, Sakyo-ku, Kyoto 606-8502, Japan
30. Current address: Department of Chemistry, Graduate School of Science, Kyoto University, Kitashirakawa-Oiwakecho, Sakyo-ku, Kyoto 606-8502, Japan
31. Current address: Department of Chemistry, Graduate School of Science, Kyoto University, Kitashirakawa-Oiwakecho, Sakyo-ku, Kyoto 606-8502, Japan
32. Current address: Department of Chemistry, Graduate School of Science, Kyoto University, Kitashirakawa-Oiwakecho, Sakyo-ku, Kyoto 606-8502, Japan
33. Current address: Department of Chemistry, Graduate School of Science, Kyoto University, Kitashirakawa-Oiwakecho, Sakyo-ku, Kyoto 606-8502, Japan
34. Current address: Department of Chemistry, Graduate School of Science, Kyoto University, Kitashirakawa-Oiwakecho, Sakyo-ku, Kyoto 606-8502, Japan
35. Current address: Department of Chemistry, Graduate School of Science, Kyoto University, Kitashirakawa-Oiwakecho, Sakyo-ku, Kyoto 606-8502, Japan
36. Current address: Department of Chemistry, Graduate School of Science, Kyoto University, Kitashirakawa-Oiwakecho, Sakyo-ku, Kyoto 606-8502, Japan
37. Current address: Department of Chemistry, Graduate School of Science, Kyoto University, Kitashirakawa-Oiwakecho, Sakyo-ku, Kyoto 606-8502, Japan
38. Current address: Department of Chemistry, Graduate School of Science, Kyoto University, Kitashirakawa-Oiwakecho, Sakyo-ku, Kyoto 606-8502, Japan
39. Current address: Department of Chemistry, Graduate School of Science, Kyoto University, Kitashirakawa-Oiwakecho, Sakyo-ku, Kyoto 606-8502, Japan
40. Current address: Department of Chemistry, Graduate School of Science, Kyoto University, Kitashirakawa-Oiwakecho, Sakyo-ku, Kyoto 606-8502, Japan
41. Current address: Department of Chemistry, Graduate School of Science, Kyoto University, Kitashirakawa-Oiwakecho, Sakyo-ku, Kyoto 606-8502, Japan