

# **Au(core)/Pd(shell) Structures Analyzed by High-resolution Medium Energy Ion Scattering**

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## **Abstract**

Bimetallic nano-particles taking a core/shell structure dispersed on metal-oxide supports work more efficiently than the mono-metallic ones as heterogeneous catalyst. In order to elucidate the high catalytic activities, it is essential to analyze quantitatively the size and structure of the core/shell particles. Here, we demonstrate that high-resolution medium energy ion scattering (MEIS) spectrometry makes it possible to identify growth of bimetallic core/shell nano-particles and also to determine the average size of core and shell, respectively together with the size distribution with an accuracy better than 0.1 nm. As an example, Au(core)-Pd(shell) particles with a nominal size (outer diameter) of 2.4 and 3.7 nm prepared by an alcohol reduction technique were analyzed using 120 keV He<sup>+</sup> ions. The present analysis clearly showed formation of Au(core)-Pd(shell) structures with almost the same radii as those expected from the chemical preparation condition. Growth of Au/Pd alloyed particles and significant inclusion of Au and Pd mono-metallic particles were ruled out.

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## 1. Introduction

Up to now, metal nano-particles grown on oxides supports have attracted much attention as heterogeneous catalyst[1]. It has been shown that the smaller the particle size, the stronger the catalytic activities[2,3]. The technique to control the size and uniformity has been developed remarkably and nowadays the growth of nano-particles with a uniform size of ~2 nm has been achieved[4,5]. Recently, it is also revealed that bimetallic core/shell particles exhibit higher catalytic activities than the constituent mono-metallic particles[6,7]. Now we need to characterize quantitatively core/shell particles with a size less than 5 nm, which cannot be viewed by a conventional transmission electron microscope (TEM). Actually high energy electron beams can be focused into a small size down to ~0.5 nm but a line scan using such a focused electron beam frequently breaks and changes the structures of core/shell nano-particles.

This paper demonstrates that high-resolution medium energy ion scattering (MEIS) spectrometry allows us to identify the growth of core/shell particles and also to determine the average size and the size distribution with an accuracy better than 0.1 nm for Au(core)/Pd(shell) with an outer diameter from 1 to 5 nm. The Au(core)/Pd(shell) particles were prepared by alcohol reduction at 100°C and the surfaces were protected with poly-N-vinyl-2-pyrrolidone(PVP) molecules[6]. We put the droplets of the solution containing the core/shell particles onto ZnS(001) and highly-oriented pyrolytic graphite (HOPG) and dried the sample at room temperature (RT). The PVP molecules were eliminated by dip into alcohol and then into de-ionized water. After that the sample was dried in nitrogen ambience at RT and then immediately introduced into an ultra-high vacuum chamber for MEIS analysis. The absence of PVP molecules was confirmed from the energy positions of the front edges for the scattering components from Pd and Au in MEIS spectra. It was revealed that ZnS substrates work more effectively to retain the core/shell particles rather than HOPG. We used 120 keV He<sup>+</sup> ions well collimated in the horizontal plane (0.17 mm) and scattered He<sup>+</sup> ions were detected by a toroidal electrostatic analyzer (ESA) with an excellent energy resolution of  $9 \times 10^{-4}$ [8]. The detail of the toroidal ESA was described elsewhere[9].

## 2. Experiment

The structure of core/shell particles is analyzed in such a way that the observed MEIS spectrum is reproduced by constructing a spectrum assuming a co-centric partial sphere as the shape of the core/shell particles with average outer and inner diameters of  $d_1$  and  $d_2$  and height  $h$  which take a normal distribution. In the present analysis we assumed a sphere as the particle shape, because the core/shell particles were loosely bound to the ZnS(001) substrates. In the MEIS spectrum simulation, the core/shell taking a sphere was subdivided into a number of small cubes with a side length of 0.05 – 0.1 nm[10] and the spectrum shape dependent upon the side length was checked in advance. The present analysis method is basically similar to that applied to Au nano-particles[10].

If a scattering geometry (incident and detection angles) is appropriately set, the incoming and outgoing path lengths for a scattered ion from each cube are easily calculated. We assumed the stopping power of  $1.0 \times S_Z(E)$  for Pd and used the relation of  $1.1 \times S_Z(E)$  for Au ( $E$ : He ion energy,  $S_Z(E)$ : Ziegler's semi-empirical stopping power formula[11]), which was previously measured using an Au thin film (~3 nm) stacked on a slightly oxidized Si substrate. The Lindhard-Scharff formula[12] was employed for energy straggling  $\Omega_{LS}$  and an exponentially modified Gaussian profile was applied as an asymmetric line shape[13] for the scattering component from each small cube, which is expressed below:

$$f(E_{out}(n) - E) = \frac{1}{2\sigma_0} \exp\left[-\frac{1}{2\sigma_0} \left\{ 2(E_{out}(n) - E) - \frac{\Omega_n^2}{\sigma_0} \right\}\right] \left\{ 1 + \operatorname{erf}\left(\frac{E_{out}(n) - E - \Omega_n^2 / \sigma_0}{\sqrt{2}\Omega_n}\right) \right\}, \quad (1)$$

where  $E_{out}(n)$ ,  $\Omega_n$ , and  $\sigma_0$  are emerging energy and energy spread of  $\text{He}^+$  scattered from  $n$ -th cube and an asymmetric parameter, respectively[13,14]. The  $\sigma_0$  values used here are 170 eV for Au and 150 eV for Pd[14]. The energy spectrum for  $\text{He}^+$  ions scattered from metal atoms  $j$  in the  $n$ -th cube (volume:  $v$ ) is given by

$$Y_n^j(E) = Q f(E_{out}^j(n) - E) (d\sigma_j / d\Omega)_n \Delta\Omega c_j v \varepsilon \eta_+, \quad (2)$$

where  $Q$ ,  $(d\sigma_j / d\Omega)_n$ ,  $c_j$ ,  $\Delta\Omega$ ,  $\varepsilon$ , and  $\eta_+$  are number of incident particles, differential scattering cross section and number density of atom  $j$ , solid angle subtended by the detector (known), detection efficiency ( $\varepsilon = 0.44$ ), and  $\text{He}^+$  fraction, respectively. The scattering cross sections were calculated numerically using the screened Coulomb potential (ZBL)[11]. The  $\text{He}^+$  fractions dependent on emerging energy and angle were measured for Au(~1 nm)/Ni(111). Finally, we obtain the total energy spectrum by convoluting each spectrum from all the cubes and constituent elements (Au and Pd).

### 3. Results and Discussion

Figure 1(a) shows the MEIS spectrum measured for Au(core)/Pd(shell) particles with a Pd/Au ratio of 1/1 (preparation condition) whose average outer diameter was roughly estimated to be 2.4 nm by TEM observation, which could not resolve the core/shell structure (Fig. 1(c)). The core/shell structure and the size distribution can be determined by best-fitting the simulated spectrum to the observed one, as presented before. In the present case, assumption of a sphere for all the core/shell nano-particles on ZnS(001) seems reasonable from the sample preparation procedure and thus a scattering geometry was set to an incident angle of  $-45^\circ$  and detection angle of  $+45^\circ$  with respect to surface normal. If core/shell particles take a partial sphere defined by diameter  $d$  and height  $h$ , MEIS measurements should be done under different two scattering geometries[10]. The dark yellow curve is obtained assuming a uni-modal size distribution and average core and shell diameters of 2.0 and 2.7 nm, respectively with a deviation of 25 % (FWHM). The above assumption means

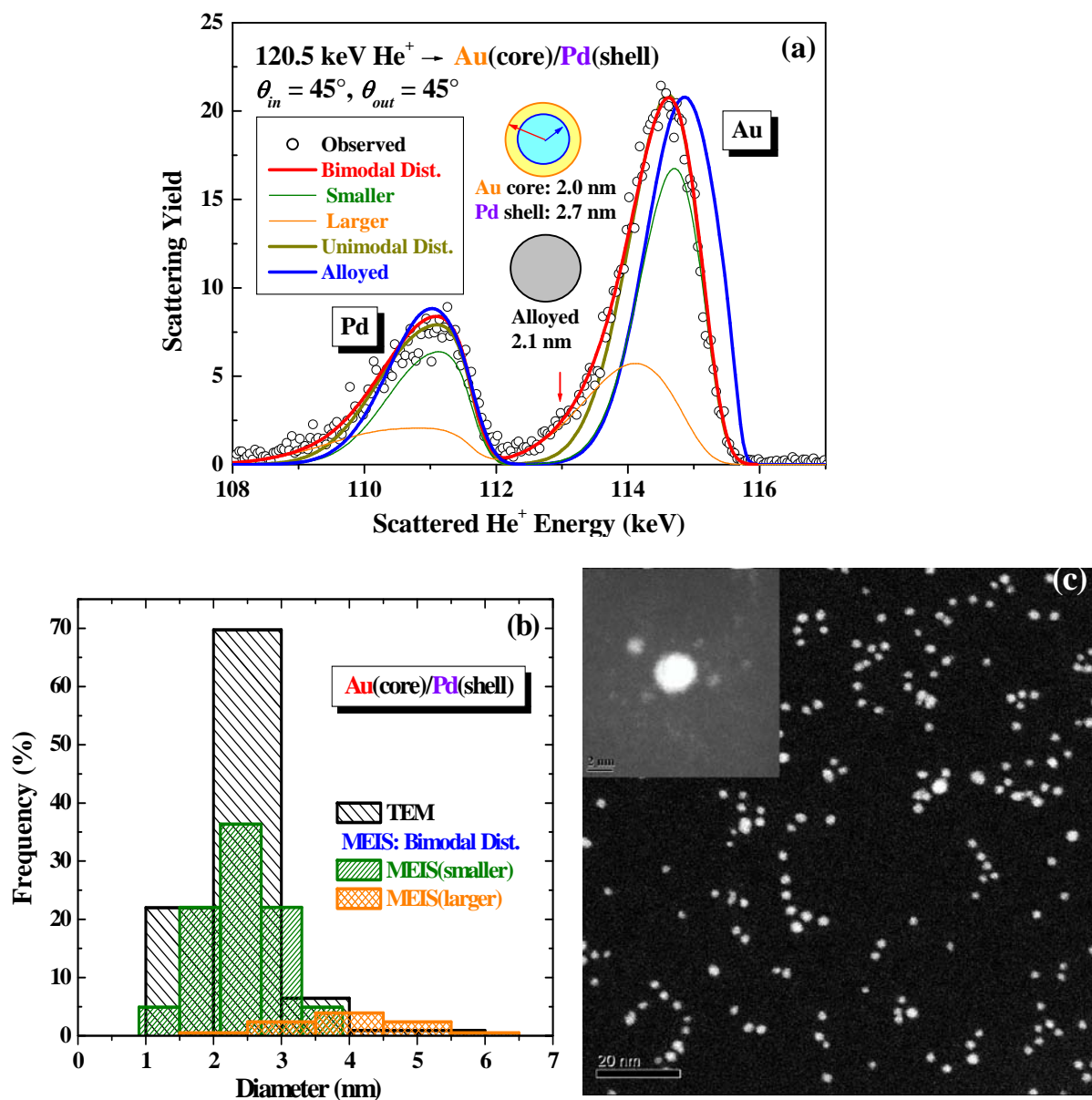


Fig. 1. (a) MEIS spectrum (circles) observed for 120.5 keV  $\text{He}^+$  incident on Pd(shell)/ Au(core) prepared by alcohol reduction technique. The thick red curve denotes the best-fit spectrum obtained by assuming Pd/Au ratio of 5/4 and the bimodal size distribution shown in Fig. 1(b). The thin green and orange curves correspond to the scattering components from a large size group and from a smaller size one, respectively. The dark yellow and blue curves are the spectra obtained assuming a uni-modal distribution (core diameter: 2.0 nm, shell diameter: 2.7 nm, size dispersion(FWHM): 25 %) and alloy formation (diameter: 2.1 nm, size dispersion(FWHM): 25 %), respectively. Here,  $\sigma_0 = 170$  eV for Au and 150 eV for Pd were used as asymmetric parameters. (c) TEM image (inset is magnified).

the Pd/Au ratio of 5/4, because the Pd and Au atomic number densities for core/shell particles were regarded as the bulk values. The chi-squared test made except for the tail region (indicated by a red

arrow in Fig. 1(a)) assures an accuracy of 0.1 nm for the average core and shell diameters. Assumption of the uni-modal size distribution does not reproduce the tail of the spectrum from Au (see a red arrow in Fig. 1(a)).

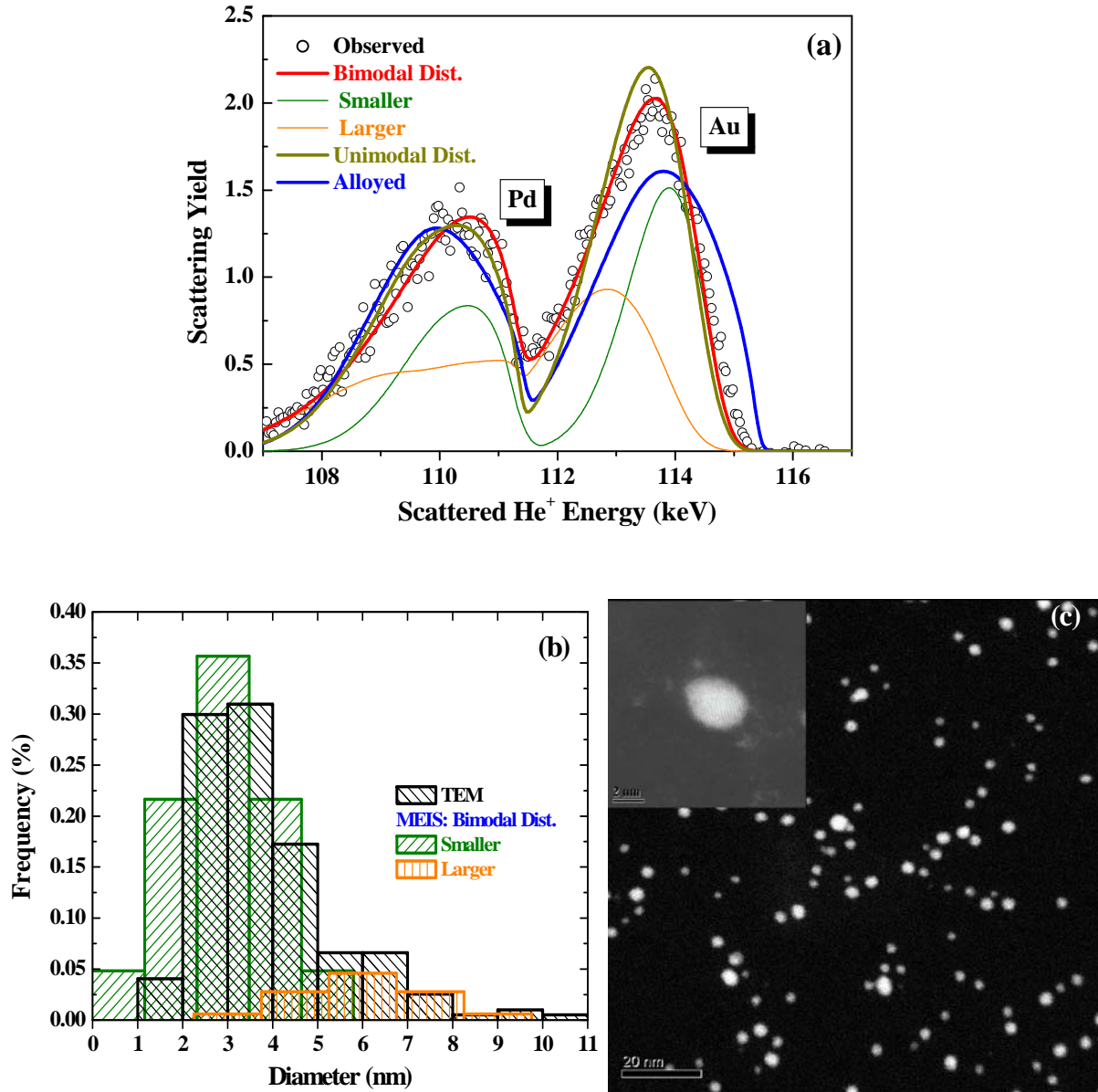


Fig. 2. (a) MEIS spectrum (circles) observed for 120.10 keV He<sup>+</sup> incident on Pd(shell)/ Au(core) particles with a size about twice that shown in Fig. 1. The thick red curve denotes the best-fit spectrum obtained by assuming Pd/Au ratio of 75/40 and the bimodal size distribution shown in Fig. 2(b). The dark yellow and blue curves are the spectra assuming a uni-modal size distribution and alloy formation, respectively. (c) TEM image (inset is magnified).

Such a bimodal size distribution as shown in Fig. 1(b) gives the best-fit spectrum (thick red curve),

although the average outer size given by TEM (black histogram) agrees with that determined by MEIS (green and orange histograms). The thin green and orange curves denote the contributions from the group with a larger size and from another one with a smaller size, respectively. It is quite interesting that no alloying takes place (see the blue curve) in spite of complete solubility of the Au-Pd system. Significant inclusion of Au and Pd mono-metallic particles are also ruled out. Another example is shown in Figs. 2(a), (b) and (c), which was measured for Pd(shell)/Au(core) particles with a larger particle size (TEM: average diameter of 3.7 nm, preparation condition: Pd/Au ratio = 6/4). Also in this case, assumption of Pd/Au ratio of 75/40 and a bimodal size distribution as shown in Fig. 2(b) give the best-fit spectrum (thick red curve). Indeed, we can see a small number of large particles in the TEM image (Fig. 2(c)). The TEM observation viewed outer diameter of particles only but could not identify the core/shell structure (see inset of Fig. 2(c)).

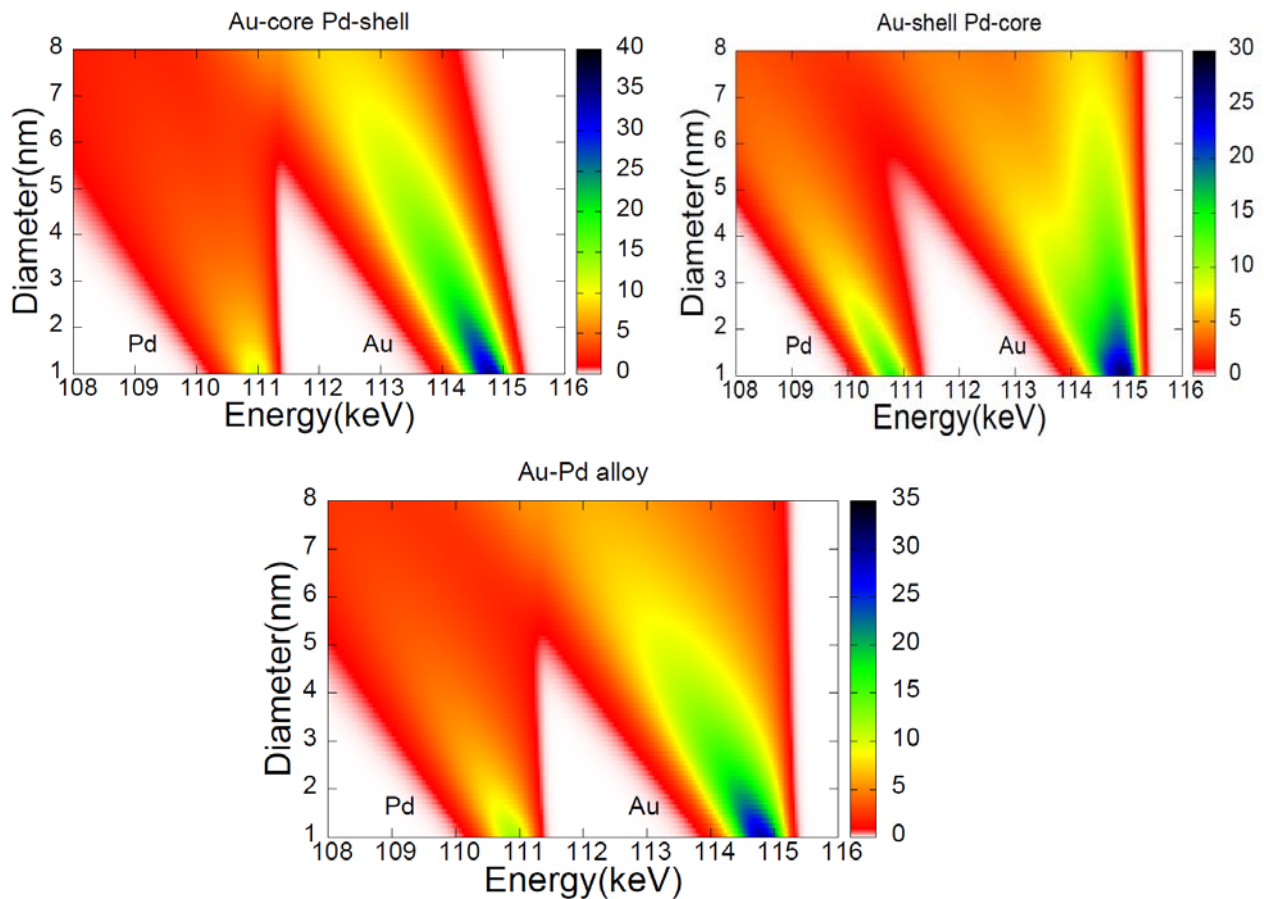


Fig. 3. Simulated MEIS spectra as a function of outer diameter assuming 120.0 keV  $\text{He}^+$  incidence, and incident and emerging angles of  $45^\circ$  for (a) Pd(shell)/Au(core) and (b) Au(shell)/Pd(core) and (c) Au-Pd alloy with a Pd/Au ratio of 1/1.

Also in this case, the average outer diameter observed by TEM agrees with that obtained by MEIS. The present MEIS spectrum simulation analysis concludes no alloying (blue curve) and no

significant inclusions of Au and Pd particles for both samples. A question may arise, whether the above best-fit condition gives the unique solution or not. Non-uniform and dispersed Au/Pd elemental composition varying with the distance from the center of the core of nano-particles may give a best-fit to the observed MEIS spectrum. However, such a complicated structure seems non-realistic and the probability should be very low.

As shown above, high-resolution MEIS allows us to confirm formation of core/shell structure and to determine the average diameters of core and shell, respectively including the size distributions. Conventional TEM observation can identify growth of core/shell particles for the size above ~5 nm by a line scan (characteristic X-ray detection: EDX) but cannot view the core/shell structures with a smaller size[15]. Extended X-ray absorption fine structure (EXAFS) analysis[6] was performed previously to determine the coordination numbers of Au and Pd, which may give an insight into which comprise the core. In spite of many efforts, it is still difficult to determine accurately the size of core and shell, respectively by other methods.

Figures 3(a) and (b) show the simulated energy spectra as a function of outer diameter for Pd(shell)/Au(core) and Au(shell)/Pd(core) particles ( $\text{Pd/Au} = 1/1$ ), respectively at 120 keV  $\text{He}^+$  incidence (incident angle:  $45^\circ$ , emerging angle:  $45^\circ$ ). Here, the size dispersion is not considered for simplicity. As clearly seen, the energy width for each scattering component from Au and Pd correlated with the core and shell diameters. The pictures indicate that our MEIS analysis is available for outer diameter below 5 nm. For larger particles size, the spectrum from Au overlaps that from Pd. In the case of Pt/Au core/shell particles, it is impossible to resolve the scattering components from Pt and from Au because of the close mass numbers. Figure 3(c) indicates the energy spectra as a function of a diameter for Au-Pd alloyed particles ( $\text{Pd/Au} = 1/1$ ). From these figures, we can easily judge which grows, Pd(shell)/Au(core), Au(shell)/Pd(core), or alloy from the energy positions of the front edges for the scattering components from Au and Pd.

#### 4. Summary

In summary, it is shown that high-resolution MEIS makes it possible to confirm clearly growth of core/shell structures and simultaneously to determine the average sizes of the core and shell, respectively together with the size distribution. Alloy formation and significant inclusion of mono-metallic particles are also detectable. The present MEIS analysis is available for the Pd(shell)/Au(core) and Au(shell)/Pd(core) nano-particles with a size ranging from 1 to 5 nm, which cannot be characterized by conventional TEM techniques.

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## References

- [1] H.J.- Freund, Surf. Sci. **500** (2002) 271.
- [2] M. Haruta, Catal. Today **36** (1997) 153.
- [3] M. Valden, X. Lai, and D.W. Goodman, Sci. **281** (1998) 1647.
- [4] H. Tsunoyama, H. Sakurai, and T. Tsukuda, Chem. Phys. Lett. **429** (2006) 528.
- [5] T. Fujitani, I. Nakamura, T. Akita, M. Okumura, and M. Haruta, Angew. Chem. Int. Ed. **48** (2009) 9515.
- [6] N. Toshima, M. Harada, Y. Yamazaki, and K. Asakura, J. Phys. Chem. **96** (1992) 9927.
- [7] D.I. Enache, J.K. Edwards, P. Landon, B. Solsona-Espriu, A.F. Carley, A.A. Herzing, M. Watanabe, C.J. Kiely, D.W. Knight, G.J. Hutchings, Science **311** (2006) 362.
- [8] Y. Kido, T. Nishimura, Y. Hoshino, and H. Namba, Nucl. Instrum. Methods **B 161-163** (2000) 371.
- [9] T. Nishimura, A. Ikeda, and Y. Kido, Rev. Sci. Instrum. **69** (1998) 1671.
- [10] A. Iwamoto, T. Okazawa, T. Akita, I. Vickridge, and Y. Kido, Nucl. Instrum. Methods **B 266** (2008) 965.
- [11] J.F. Ziegler, J.P. Biersack and U.L. Littmark, *The Stopping and Range of Ions in Solids* (Pergamon Press, New York, 1985).
- [12] J. Lindhard and M. Scharff, K. Dan. Vidensk. Selsk. Mat. Fys. Medd. **27**, 15 (1953).
- [13] P.L. Grande, A. Hentz, R.P. Pezzi, I.J.R. Baumvol, G. Schiwietz, Nucl. Instrum. Methods **B 256** (2007) 92.
- [14] M. Hazama, Y. Kitsudo, T. Nishimura, Y. Hoshino, P.L. Grande, G. Schiwietz, and Y. Kido, Phys. Rev. **B 78** (2008) 193402.
- [15] T. Akita, T. Hiroki, S. Tanaka, T. Kojima, M. Kohyama, A. Iwase, and F. Hori, Catal. Today **131** (2008) 90.