Quantitative Evaluation of the Composition of Au-Pd nanoparticles Using Neutron Activation Analysis

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Abstract

In the synthesis and application of nanoparticles, quantitative analysis of the components of the synthesized nanoparticles is very important because it is criterion for judging the validity of the synthesis method. The primary methods used to quantify nanoparticle composition include Inductively coupled plasma mass spectrometry (ICP-MS) and neutron activation analysis (NAA), ICP-MS is typically used for the qualitative and quantitative evaluation of the composition of synthesized nanoparticles, but the pretreatment process required to prepare the analytical sample is relatively complex and demanding. NAA has become a highly sensitive method for analyzing multiple elements today. The technique can retrieve both quantitative and qualitative data for individual elements, with sensitivities that exceed those achievable with other analytical methods. In what's more, sample preparation is relatively simple and the method is non-destructive. The aim of this study was to apply NAA to the composition ratio analysis of Au-Pd nanoparticles synthesized at different ratios and to evaluate the results.

Synthesis of Au-Pd alloy nanoparticles

The Au-Pd alloy nanoparticles were synthesized by a modified Turkevich method with different Pd concentrations. (fig.1) Each Au-Pd alloy nanoparticle was synthesized by making a stock solution of 0.1 mM of $HAuCl_4$ and H_2PdCl_4, the content of Pd was 0.01, 0.02, 0.05, 0.1 and 0.2%, respectively, and the total amount of reaction solution was equalized. The changes in the synthesis solution before and after the reaction, TEM images showing the morphology of the synthesized nanoparticles, and EDX analysis results showing the composition of the synthesized nanoparticles are shown in Figure 2.

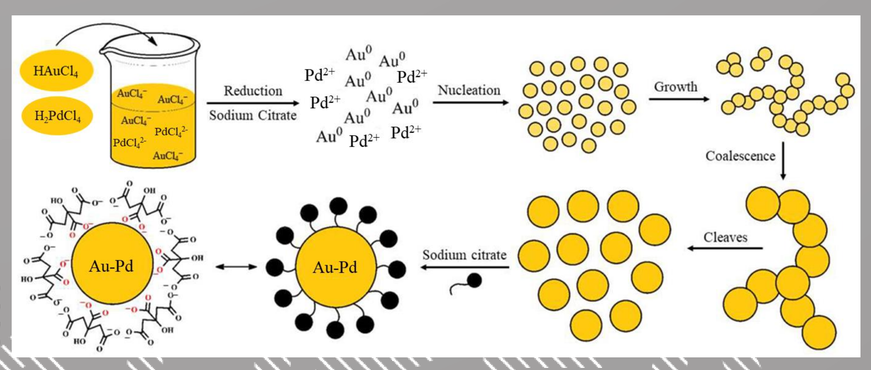


Fig.1 Scheme of the Au-Pd alloy nanoparticles synthesis process.

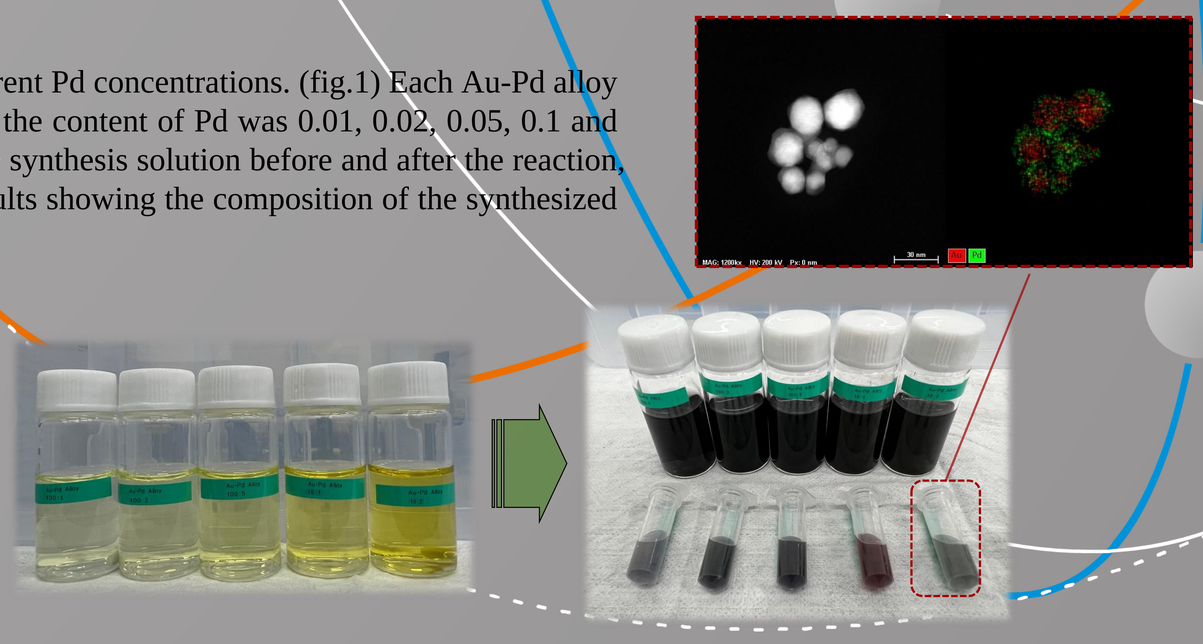


Fig.2 Photographs of before (left) and after (right) the synthesis and TEM & EDX image.

NAA simulation

In order to apply the analysis using NAA, it is necessary to evaluate the gamma rays emitted after neutron irradiation. Therefore, to evaluate NAA before applying it to the composition analysis of Au-Pd nanoparticles, we performed simulations using the program "NAA Pro". The NAA simulation were performed using a total 10 mg of sample and applying the neutron flux shown in fig.3. The simulation results are shown in Fig, 4 and Fig. 5.

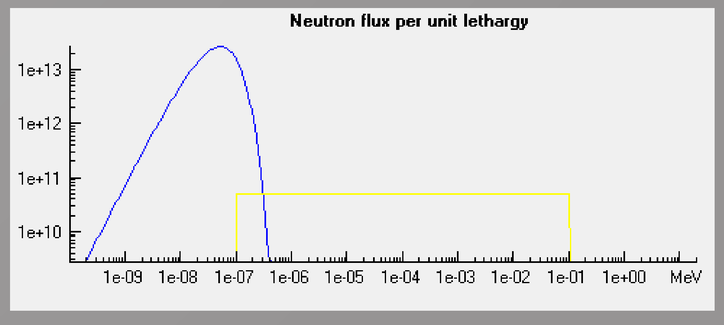
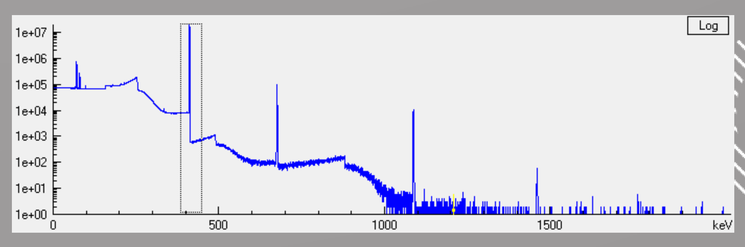
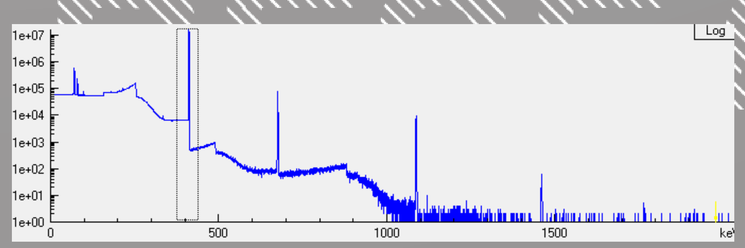


Fig.3 Neutron flux applied to the simulation



		Gamma ray (keV)	Activity (MBq)					
			10s	20s	30s	40s	50s	60s
Pure Gold	Au-198	411.802	4.036E+00	8.071E+00	1.211E+01	1.614E+01	2.018E+01	2.421E+01
	Au-198m1	214.89	2.411E-03	4.823E-03	7.234E-03	9.645E-03	1.206E-02	1.447E-02
	Au-19	158.379	1.904E-05	7.615E-05	1.713E-04	3.046E-04	4.759E-04	6.853E-04

Fig.4 Simulation result of pure gold



		Gamma ray (keV)	Activity (MBq)					
			10s	20s	30s	40s	50s	60s
Au:Pd 99.9:0.01	Ag-109m1	22.163	6.714E-05	1.382E-04	2.074E-04	2.766E-04	3.457E-04	4.149E-04
	Ag-111m1	22.163	2.143E-05	4.276E-05	6.399E-05	8.537E-05	1.065E-04	1.275E-04
	Au-198	441.802	4.031E+00	8.063E+00	1.207E+01	1.613E+01	2.016E+01	2.419E+01
	Au198m1	214.89	2.409E-03	4.818E-03	7.226E-03	9.635E-03	1.204E-02	1.445E-02
	Au-199	158.379	1.902E-05	7.607E-05	1.172E-04	3.043E-04	4.754E-04	6.846E-04
	Pd-103	20.216	3.775E-08	7.550E-08	1.133E-07	1.510E-07	1.888E-07	2.265E-07
	Pd-107m1	214.3	8.136E-13	1.401E-12	1.826E-12	2.132E-12	2.353E-12	2.513E-12
	Pd-109	311.4	6.918E-05	1.384E-04	2.075E-04	2.767E-04	3.459E-04	4.150E-04
	Pd109m1	188.9	5.973E-05	1.180E-04	1.749E-04	2.303E-04	2.845E-04	3.373E-04
	Pd-111	580	2.054E-05	4.133E-05	6.155E-05	8.186E-05	1.021E-04	1.222E-04
	Pd-111m1	172.18	3.744E-07	7.487E-07	1.123E-06	1.497E-06	1.871E-06	2.245E-06

Fig.5 Simulation result of the Au:Pd nanoparticle composed in a ratio of 99.99:0.01

Table.1 Average neutron Fluxes and Cadmium Ratio Measured at each NAA Irradiation Holes (30 MW)

	Average Thermal neutron flux (n/cm²) (30 MV)			Cadmium ratio (Au)
	Thermal, ϕ_t	Epithermal, ϕ_e	Fast, ϕ_f	
NAA 1 (PTS#1)	$4.80\pm0.02 \times 10^{13}$	$7.80\pm0.22 \times 10^{11}$	$6.38\pm0.49 \times 10^{10}$	48±2
NAA 2 (PTS#2)	$3.30\pm0.09 \times 10^{13}$	$3.44\pm0.29 \times 10^{11}$	$3.27\pm0.47 \times 10^{10}$	100±2
NAA 3 (PTS#3)	$1.53\pm0.06 \times 10^{14}$	$1.01\pm0.07 \times 10^{12}$	$9.78\pm0.05 \times 10^{11}$	10±1

Neutron Activation

The synthesized nanoparticles were weighed for neutron activation analysis and irradiated with neutrons using a HANARO neutron irradiation system (pneumatic transfer system, PTS) as shown in Fig.6. Neutron irradiation was performed for 1 minute for each sample using the PTS#1 hole, and the neutron flux at the NANARO neutron irradiation facility as shown in Table.1.

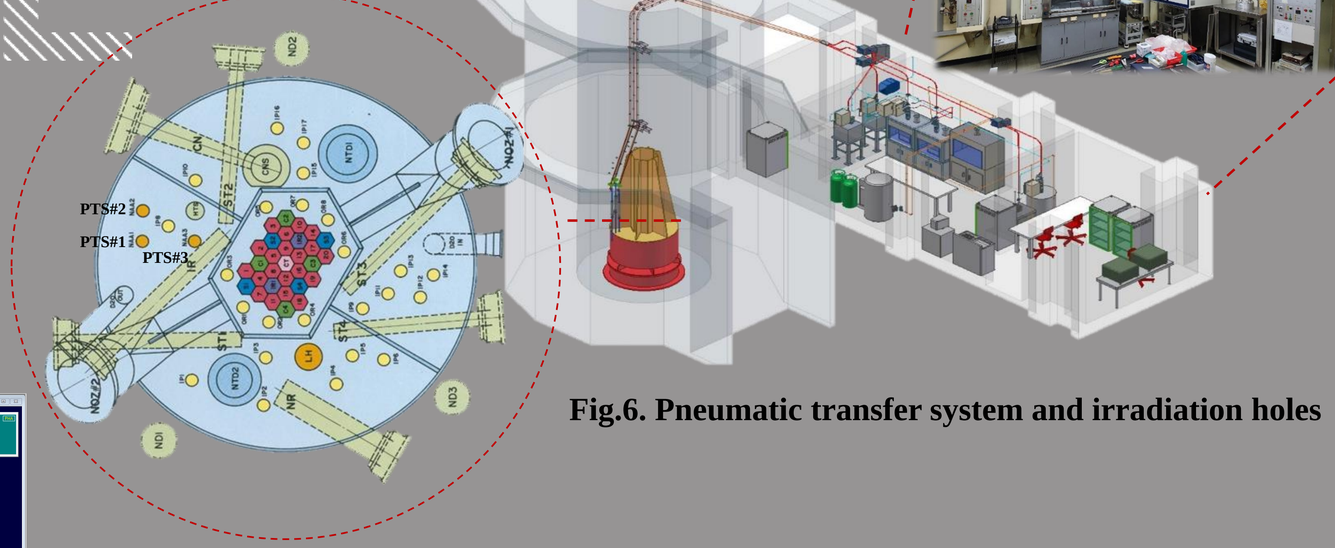


Fig.6. Pneumatic transfer system and irradiation holes

Quantitative analysis

The neutron-activated samples were quantitatively analyzed for each component by measuring their respective spectra as shown in Fig.7.

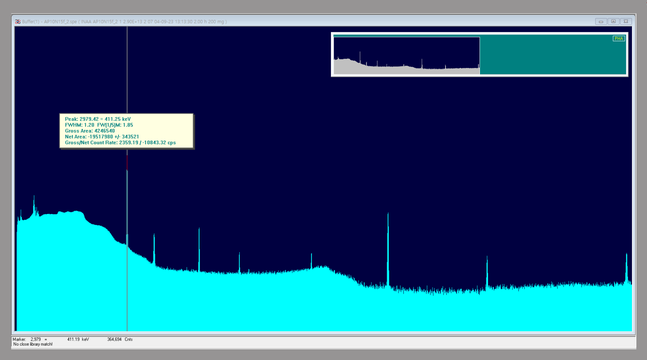


Fig.7. Spectrum of a neutron-activated sample.

Conclusion

Further quantitative analysis is currently being performed based on the measured spectra, and additional analysis experiments will be conducted by changing the neutron irradiation conditions.

Acknowledgement

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