

# CALORIMETRIC STUDY ON SELF-ASSEMBLING OF TWO KINDS OF MONOMETALLIC NANOPARTICLES IN SOLUTION

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Recently, we have reported a noble method of preparing Ag/Rh bimetallic nanoparticles with a pseudo-core/shell structure. We simply mix the dispersions of poly(*N*-vinyl-2-pyrrolidone)(PVP)-protected Ag and Rh nanoparticles in solution at room temperature. We found that the mixture of dispersions forms bimetallic nanoparticles in a pseudo-core/shell structure on standing. We call this process the 'self-assembling' or 'self-organizing'. In this study we seek for a thermodynamic driving force for this process by determining the enthalpy of the interaction among three pairs of nanoparticles by isothermal titration calorimetry (ITC). The results indicate that the interaction between each pair is strongly exothermic, and that among the pairs studied here the strength of the exothermic interaction is in the order of Ag/Pt < Ag/Pd < Ag/Rh.

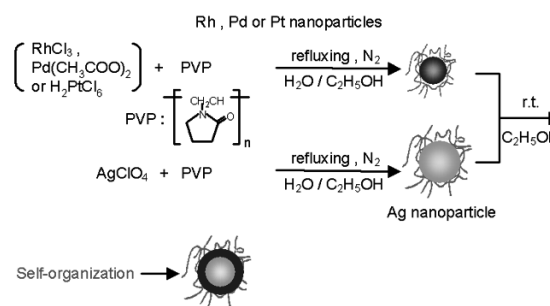
**Keywords:** bimetallic nanoparticles, calorimetric method, core/shell structure, isothermal titration calorimetry, metal nanoparticle, palladium, platinum, rhodium, self-assembling, self-organization, silver

## Introduction

Recently much attention has been paid to bimetallic nanoparticles for applications in the fields of catalysis, magnetism, optics, etc. [1–3]. For these applications, bimetallic nanoparticles, in which each particle is composed of two kinds of metal elements, become more important year by year [4–6]. The bimetallic nanoparticles have several kinds of structures, such as random alloy (solid solution type), cluster-in-cluster, layered structure, core/shell structure, and so on. Structural control of bimetallic nanoparticles is one of the important issues for the researchers on metal nanoparticles. For example, the core/shell structure of Pd/Pt bimetallic nanoparticles, prepared by a simultaneous reduction of both metal ions with refluxing alcohol, was first proved by an extended X-ray absorption fine structure (EXAFS) technique in 1991 by the present authors [7]. Since then many examples of preparation of core/shell-structured bimetallic nanoparticles have been reported by simultaneous reduction not only with refluxing alcohol [4–6, 8–12] but also with sonochemical reaction and so on [13–19]. A sacrificial hydrogen reduction method was also developed to control the core/shell structure [20]. Recently we have found that physical mixing of poly(*N*-vinyl-2-pyrrolidone)(PVP)-protected Ag nanoparticles with PVP-protected Rh nanoparticles in solution at room temperature can produce a pseudo-core/shell

structure by self-organization, as shown in Fig. 1 [21]. At first sight, this is a very peculiar and interesting phenomenon. This kind of formation of core/shell-structured bimetallic nanoparticles just by mixing the constituent metal nanoparticles had never been reported before. It could be probable because nanoparticles can be so reactive as to behave like metal atoms. However, the thermodynamic or kinetic aspects of this self-organization reaction are not known at all.

Isothermal titration calorimetry (ITC) is a sensitive technique that measures the heat of reaction of two solutions when one is titrated against the other. It became a powerful tool for studying the thermodynamic as well as kinetic aspects of interaction of chemical species in solution. Aside from a recent study on binding of DNA bases to nanoparticles [22],



**Fig. 1** Preparation of bimetallic nanoparticles by mixing of two kinds of monometallic nanoparticles prepared independently by refluxing in water/ethanol

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to our knowledge, ITC has never been applied for metal nanoparticle research.

Here we examine the interaction between PVP-protected Ag nanoparticles and three kinds of noble metals (Rh, Pd and Pt) nanoparticles by ITC for the first time. The results reveal a strong exothermic interaction between those nanoparticles.

## Experimental

### Materials

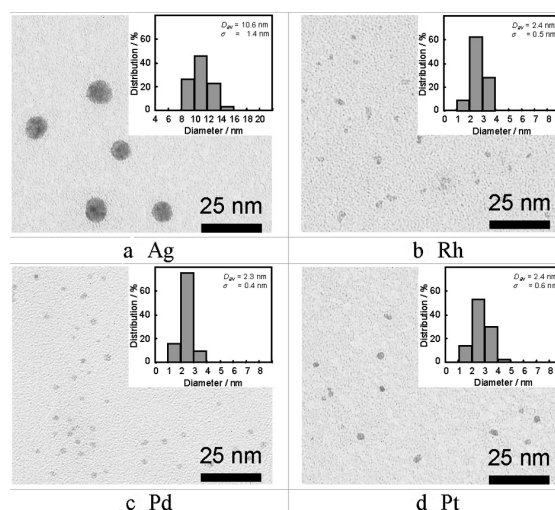
Silver perchlorate and palladium(II) acetate were received from Kojima Chemicals Co., Ltd. Rhodium(III) chloride, hexachloroplatinic(IV) acid and ethanol were supplied by Wako Pure Chemical Industries, Ltd. Poly(*N*-vinyl-2-pyrrolidone) (PVP, K-30, average molecular mass 40,000; Wako Pure Chemical Industries, Ltd.) was used without further purification as the protective polymer for metal nanoparticles.

### Preparation of metal nanoparticles

A typical procedure [23] to prepare polymer-protected monometallic nanoparticles is as follows: A solution of noble-metal salts (silver perchlorate, rhodium(III) chloride, palladium(II) acetate or hexachloroplatinic(IV) acid) (0.66 mM) in 500 mL of ethanol/water (1/9, *v/v*) was heated with refluxing for a few hours under nitrogen in the presence of PVP (13.2 mmol) as protecting polymer. PVP-protected metal nanoparticles thus prepared were purified by filtration with ultra filter to remove byproduced ions and then dried under vacuum. The dried metal nanoparticles were dispersed in pure ethanol. Dispersions of the Ag and noble metal (Rh, Pd or Pt) nanoparticles, prepared separately with the same concentration of PVP, were mixed to form bimetallic at room temperature, the process of which was followed by ITC.

### Measurements

Ultraviolet and visible (UV-Vis) spectra were obtained at room temperature using a Shimadzu 2500PC recording spectrophotometer equipped with a 10 mm quartz cell. Transmission electron microscopy (TEM) was used to characterize the monometallic and bimetallic nanoparticles employed here. For this purpose we used a JEOL JEM-1230 electron microscope operated at 80 kV. Samples for TEM measurement were prepared by placing a drop of the colloidal dispersion of metal nanoparticles onto a carbon-coated copper microgrid, followed by naturally evaporating the solvent. The mean diameter and standard deviation were calculated by counting the diameters of ca. 200 parti-



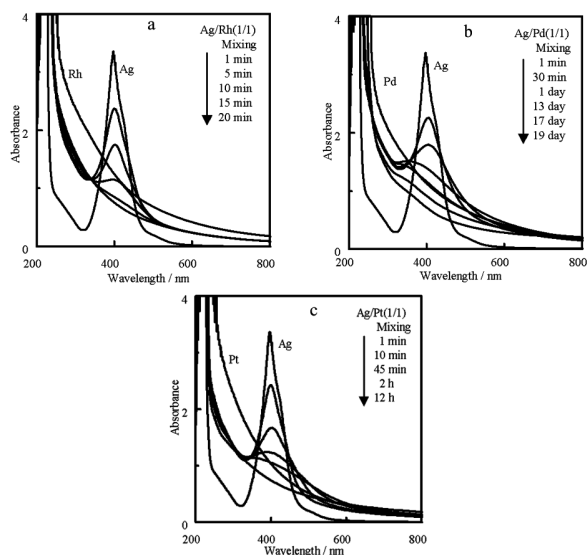
**Fig. 2** Transmission electron micrographs and particle size distribution histograms of noble metal nanoparticles: a – PVP-Ag, b – PVP-Rh, c – PVP-Pd, d – PVP-Pt.  $D_{av}$ =average diameter,  $\sigma$ =standard deviation

cles with a magnifier (10 times) on the TEM photograph of 100,000 magnifications. Isothermal titration calorimetric (ITC) experiments were performed using a MicroCal MCS-ITC instrument at 30°C, wherein 50 mL of a 0.66 mM ethanol solution of metal nanoparticle dispersions were injected in equal steps of 2.5 mL into 1.34 mL of a 0.66 mM ethanol solution of another nanoparticle dispersion. All the samples used for calorimetric measurement were purified by removing the byproducts, produced during the preparation of metal nanoparticles, with an Ultra Filter separation system.

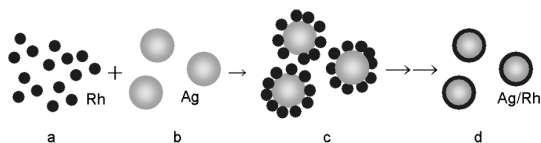
## Results and discussion

### Formation of core/shell-structured bimetallic nanoparticles

Transformation of metal ions to dispersions of monometallic nanoparticles was confirmed by disappearance of bands attributed to metal ions in UV-Vis absorption spectra. Based on the TEM observation of the produced dispersions, the Ag, Rh, Pd, and Pt nanoparticles are reasonably monodispersed and have the average diameters of 10.6, 2.4, 2.3 and 2.4 nm, respectively, as Fig. 2 shows. When the dispersions of Ag and noble metal nanoparticles are mixed at a molar ratio of 1:1, the surface plasmon absorption at near 420 nm, which is characteristic of Ag nanoparticles, gradually disappears with progress of time, as shown in Fig. 3. This observation has suggested that the surface of Ag nanoparticles (Fig. 4b) is covered with Rh nanoparticle (Fig. 4a) to form pseudo-core/shell-structured bimetallic nanoparticles (Fig. 4c). This



**Fig. 3** Quenching of Ag surface plasmon absorption by addition of noble metal nanoparticles

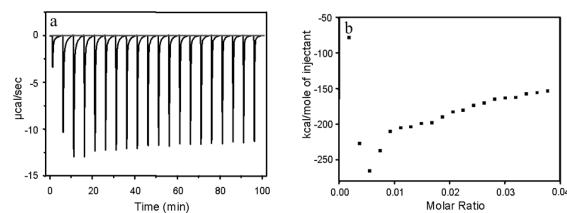


**Fig. 4** Schematic presentation of formation of Ag-core/Rh-shell structures by mixing dispersions of Rh and Ag nanoparticles

kind of gathered structures were also observed in TEM photographs after mixing Ag and Rh nanoparticles [21]. Recently we have found that the aggregate structures can be rearranged just by keeping the mixed dispersions at room temperature to form a reasonably monodispersed core/shell-structured bimetallic nanoparticles (Fig. 4d) with a smaller size than the original Ag nanoparticles. Details will be published elsewhere.

#### *Calorimetric measurement of an interaction between silver and noble metal nanoparticles*

As for the formation of pseudo-core/shell structured bimetallic nanoparticles, as shown in Fig. 4c, the first step of the reaction should be an interaction between the two monometallic nanoparticles. Thus, we evaluate the degree of interaction between the two by isothermal titration calorimetric (ITC) measurements. For this purpose, an amount of the alcoholic dispersion of PVP-protected nanoparticles of noble metal like Rh, Pd or Pt was added into the alcoholic dispersion of PVP-protected Ag nanoparticles at a constant interval. We also reversed the titrant and the titrate. The resulting ITC responses recovered during titra-



**Fig. 5** a – The calorific value per time at the time of titration of PVP-protected Rh nanoparticles into PVP-protected Ag nanoparticles and b – the relation with the injectant concentration in molar ratio

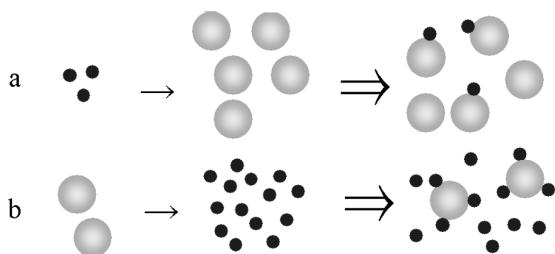
tions of PVP-protected Rh nanoparticles into PVP-protected Ag nanoparticles are shown in Fig. 5a. In order to avoid the thermal effect due to dilution with solvent the concentrations of PVP in both dispersions of Ag and Rh nanoparticles were kept constant. The heat evolved by each titration is plotted vs.  $t$  the total amount of the injectant, as shown in Fig. 5b. As is typical to ITC in general, the first data point is always of undersize due to dilution of the sample at the tip of the syringe needle. In the present case, however, it requires a few more shots before the peak size settles down. Our experience of titrating a solution of biopolymers indicates that multiple injections are necessary at times. This may hint that some rheological complication might be at work in the narrow space of syringe needle, and a number of shots of titration may be necessary to reach a steady state so that a constant volume is delivered. The colloidal dispersion is indeed notorious in this respect. While we have no precise reason for this observation, we ignore the first several points. By extrapolating the plots in Fig. 5b, the calorific value per molar injectant at the infinite dilution was calculated. The results are shown in Tables 1 and 2. Table 1 summarizes the results for calorific values between the same metal nanoparticles, indicating no interactions between the same metal nanoparticles. Even in the case of the injection of PVP-protected metal nanoparticles into PVP solution with the same concentration of PVP negligible interaction was observed. In contrast, calorific values between different kinds of metal nanoparticles are strongly exothermic, as Table 2 shows. Furthermore,

**Table 1** Molar enthalpy obtained with ITC by injecting a particle dispersion into PVP solution or the same particle dispersion

Injection particles	Particles in cell	$\Delta H/\text{kJ mol}^{-1}$
PVP-Ag	PVP+Ethanol	-4.2
PVP-Rh	PVP-Rh	-14
PVP-Pd	PVP-Pd	-5.9
PVP-Pt	PVP-Pt	-3
PVP-Ag	PVP-Ag	1.7

**Table 2** Molar enthalpy obtained with ITC by injecting a particle dispersion into another particle dispersion

Injection particles	Particles in cell	$\Delta H/\text{kJ mol}^{-1}$	$\Delta H \cdot 10^{27}/(\text{J/particle})$
PVP-Rh	PVP-Ag	-908	-0.79
PVP-Pd	PVP-Ag	-600	-0.43
PVP-Pt	PVP-Ag	-414	-0.32
PVP-Ag	PVP-Rh	-357	-21.6
PVP-Ag	PVP-Pd	-331	-21.2
PVP-Ag	PVP-Pt	-189	-11.4

**Fig. 6** The schematic of the initial state of a reaction of calorimetry measurement; a – is injecting Rh nanoparticle dispersion into Ag nanoparticle dispersion, b – is injecting Ag nanoparticle dispersion into Rh nanoparticle dispersion

the degree of exothermic interaction increases in the order of  $\text{Ag/Pt} < \text{Ag/Pd} < \text{Ag/Rh}$ . This means that the interaction between Ag and Rh nanoparticles is stronger than that between Ag and Pt or Pd.

In Table 2, we calculated also the enthalpy per particle of injectant, assuming that the density of each nanoparticle is the same as that of the bulk metal. Thus, when injectant is reversed the enthalpy of interaction per injectant particle become by some 30-fold larger. This is probably due to the size discrepancy between Ag and noble metal nanoparticles such as Rh nanoparticles. Namely, when a trace amount of small Rh nanoparticles are injected into a large amount of large Ag nanoparticles, each Rh nanoparticles can interact with only one Ag nanoparticle, as Fig. 6a shows. In contrast, a trace amount of large Ag nanoparticles are injected into a large amount of small Rh nanoparticles, Ag nanoparticles interact with a plural number of Rh nanoparticles (Fig. 6b). Thus, the results in the last column of Table 2 suggest that the total number of interaction between particles increases by some 30-fold. This argument is based on the assumption that the density of each nanoparticle is the same as that bulk metal, which is questionable in view of high reactivity of these nanoparticles. Nevertheless, the order of the exothermic interaction remains unchanged by reversing the injectant.

## Conclusions

Physical mixing of the dispersion of poly(*N*-vinyl-2-pyrrolidone)(PVP)-protected Ag nanoparticles with that of PVP-protected noble metal (Rh, Pd and Pt) nanoparticles in ethanol can produce pseudo-core/shell structured bimetallic nanoparticles, which have been confirmed by disappearance of the plasmon absorption of Ag nanoparticles with progress of time. Isothermal titration calorimetric (ITC) measurements have revealed the strong exothermic interaction between Ag nanoparticles and noble metal nanoparticles. The strength of the interaction between a pair of metals increases in the order of  $\text{Ag/Pt} < \text{Ag/Pd} < \text{Ag/Rh}$ . This strong exothermic interaction is no doubt a driving force for spontaneous formation of bimetallic nanoparticles with a pseudo-core/shell structure. The detailed mechanism is still under investigation.

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## References

- 1 G. Schmid, Clusters and Colloids From Theory to Applications, VCH, Weinheim, 1994.
- 2 N. Toshima, Encyclopedia of Nanoscience and Nanotechnology, J. A. Szwarc, C. Contescu and K. Putyera, Eds, Marcel Dekker, New York 2004, p.1869.
- 3 I. Dékány, *J. Therm. Anal. Cal.*, 79 (2005) 587.
- 4 N. Toshima and T. Yonezawa, *New J. Chem.*, 22 (1998) 1179.
- 5 T. Teranishi and N. Toshima, Catalysis and Electrocatalysis of Nanoparticle Surfaces, A. Wieckowski, E. R. Sarimone and C. C. Vayenas, Eds, Marcel Dekker, New York 2002, Chapter 11.
- 6 N. Toshima, Macromolecular Nano-Structured Materials, N. Ueyama and A. Harada, Eds., Kodansha/Springer, Tokyo/Berlin 2004, Chapter 3.3.
- 7 N. Toshima, M. Harada, T. Yonezawa, K. Kushihashi and K. Asakura, *J. Phys. Chem.*, 95 (1991) 7448.

- 8 N. Toshima, M. Harada, T. Yonezawa and K. Asakura, *J. Phys. Chem.*, 96 (1992) 9927.
- 9 T. Yonezawa and N. Toshima, *J. Mol. Catal.*, 83 (1993) 167.
- 10 T. Yonezawa and N. Toshima, *J. Chem. Soc. Faraday Trans.*, 91 (1995) 4111.
- 11 N. Toshima, T. Yonezawa and K. Kushihashi, *J. Chem. Soc., Faraday Trans.*, 84 (1993) 2573.
- 12 M. Harada, K. Asakura, Y. Ueki and N. Toshima, *J. Phys. Chem.*, 96 (1992) 9730.
- 13 Y. Mizukoshi, T. Fujimoto, Y. Nagata, R. Oshima and Y. Maeda, *J. Phys. Chem. B*, 104 (2000) 6028.
- 14 C. Kan, W. Cai, C. Li, L. Zhang and H. Hofmeiste, *J. Phys. D: Appl. Phys.*, 36 (2003) 1609.
- 15 S. Mandal, A. B. Mandale and M. Sastry, *J. Mater. Chem.*, 14 (2004) 2868.
- 16 H. Tada, F. Suzuki, S. Ito, T. Akita, K. Tanaka, T. Kawahara and H. Kobayashi, *J. Phys. Chem. B*, 106 (2002) 8714.
- 17 J. Park and J. Cheon, *J. Am. Chem. Soc.*, 123 (2001) 5743.
- 18 J. H. Hodak, A. Henglein and G. V. Hartland, *J. Chem. Phys.*, 114 (2001) 2760.
- 19 M. S. Nashner, A. I. Frenkel, D. Somerville, C. W. Hills, J. R. Shapley and R. G. Nuzzo, *J. Am. Chem. Soc.*, 120 (1998) 8093.
- 20 Y. Wang and N. Toshima, *J. Phys. Chem. B*, 101 (1997) 5301.
- 21 K. Hirakawa and N. Toshima, *Chem. Lett.*, 32 (2003) 78.
- 22 A. Gouriskaukar, S. Shukle, K. N. Ganesh and M. Sastry, *J. Am. Chem. Soc.*, 126 (2004) 13186.
- 23 H. Hirai, Y. Nakano and N. Toshima, *J. Macromol. Sci. Chem.*, A13 (1979) 727.

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