Electronic Supplementary Information

Rapid spontaneous alloying between Pd nanocubes and Ag nanoparticles in aqueous solution at ambient temperature

Masaharu Tsuji,*[a,b,c] Chihiro Shiraishi,[b] Masashi Hattori,[a] Atsuhiko Yajima,[b] Masahito Mitarai,[d] Keiko Uto,[a] Koichi Takemura[b] and Yukinori Nakashima[b]

[a] *Institute for Materials Chemistry and Engineering, Kyushu University, Kasuga 816-8580, Japan. Fax: +81-092-583-7815; Tel.: +81-092-583-7815; E-mail:tsuji@cm.kyushu-u.ac.jp*

[b] *Department of Applied Science for Electronics and Materials, Graduate School of Engineering Sciences, Kyushu University, Kasuga 816-8580, Japan*

[c] *Department of Automotive Science, Graduate School of Integrated Frontier Sciences, Kyushu University, Kasuga 816-8580, Japan*

[d] *Department of Mechanical and Control Engineering, Tokuyama College of Technology, Shunan 745-8585, Japan*

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1. Materials

For use in this study, $PdCl_2$ (>99.0%), $AgNO_3$ (>99.8%), L(+)-ascorbic acid (>99.5%), hexadecyl-trimethyl-ammonium bromide (CTAB: >99.0%), ethylene glycol (EG: >99.5%), distilled H_2O (HPLC level), 10% HCl in water, C_2H_5OH (>99.5%), PVP (average molecular weight MW = 40 k in terms of monomer units: >99.5%), trisodium citrate (Na_3CA: >99.5%), aqueous H_2O_2 solution (content 30 wt %), were purchased from Kishida Chemical Industry Ltd. These materials were used without further purification.

2. Experimental procedure: Syntheses of Pd cubes, Ag nanospheres, and triangular Ag nanoprisms.

Pd cubes, Ag nanposphes, and triangular Ag nanoprisms were prepared using reported methods.[1-3] In a synthesis of Pd cube, a 2 mL aliquot of 10 mM H_2PdCl_4 aqueous solution was added to 37.68 mL of 12.5 mM CTAB aqueous solution heated at 95 ^{o}C under stirring. After 5 min, 320 μL of freshly prepared 100 mM ascorbic acid solution was added, and then the reaction was allowed to proceed for 20 min. In this experiment, H_2PdCl_4, CTAB, and ascorbic acid are a reagent of Pd nanoparticles, a surfactant, and reducing agent, respectively. Products were centrifuged at 13000 rpm for 60 min in water to remove surfactant and other residuals in a reagent solution. Then products were dispersed in water.

Spherical Ag nanoparticles were prepared by reducing $AgNO_3$ in EG. 0.585g of PVP (MW = 40 k) was dissolved in 17.4 mL of EG. Then 2 mL of 0.465 M $AgNO_3$ EG solution was added. It was heated to a boiling point of EG (198^{o}C) and kept at this temperature for 10 min. In this experiment, $AgNO_3$ and PVP are a reagent of Ag nanoparticles and a surfactant, respectively. Products were centrifuged at 13000 rpm for 30 min two times in EG and 30 min one time in water and then redispersed in water.

Triangular prism was prepared by the addition of $NaBH_4$ solution to $AgNO_3$/PVP/citrate/H_2O_2 aqueous solution at room temperature.[3] An aqueous mixture of $AgNO_3$ (0.1 mM, 25 mL), PVP (Mw = 40 k: 0.7 mM, 1.5 mL), and Na_3CA (30 mM, 1.5 mL) was prepared. Then H_2O_2 solution (30 wt%, 0.06 mL) was added to the solution described above. Subsequently, $NaBH_4$ (100 mM, 0.14 mL) was injected to the reagent solution and the reaction was initiated. Final concentrations of $AgNO_3$, PVP, Na_3CA, H_2O_2, and $NaBH_4$ were, respectively, 0.089, 0.037, 1.60, 21, and 0.5 mM. This solution was used as spontaneous alloying experiments without centrifugal separation because Ag prisms are more easily aggregated than Ag nanospheres.

To examine effects of residual reagents used for the preparation of triangular Ag prisms, we also prepared an aqueous solution of pure Ag prisms by centrifugal separation of product solution at 13000 rpm for 30 min three times in water and then redispersed in water involving PVP (0.037 mM). No appreciable changes in TEM and UV–Vis data were obtained, indicating that residual reagents give little effects for spontaneous alloying under the present experimental conditions.

The formation of prisms from an aqueous $AgNO_3$/$NaBH_4$/PVP/Na_3CA/H_2O_2 solution proceeds through repeated oxidative etching of spherical and small plates with subsequent re-reduction of Ag^+ on side facets of plates because the top and bottom {111} facets are protected by citrate.[3] A key process for the spherical-to-prism transformation is shape-selective oxidative etching of spherical particles in a mixture of spheres and prisms. The etching rate of spherical particles by H_2O_2 is faster than that of prisms. Therefore, spherical particles are etched selectively and dissolved, leaving only seeds of prisms to grow into triangular prisms. Thus, roles of $AgNO_3$, PVP, Na_3CA, H_2O_2, and $NaBH_4$ were a reagent of Ag prisms, a surfactant of Ag nanoparticles, a special surfactant for the preparation Ag prisms by selective adsorption on {111} facets of prisms, a shape selective etchant of Ag nanoparticles, and a reducing agent, respectively.

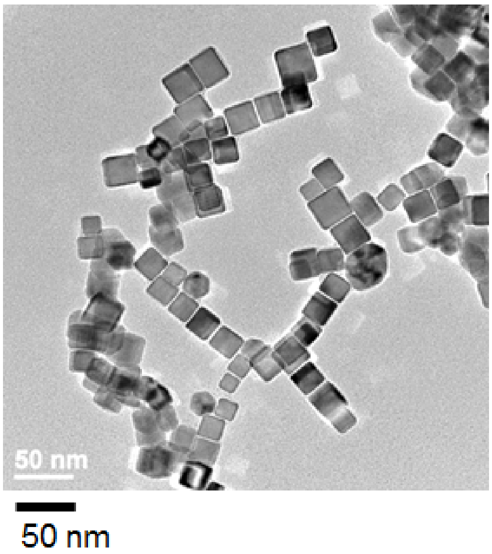
After the reaction between Pd cubes and Ag nanoparticles was completed, 1 mL of product solution diluted by 1.5 mL of ethanol was centrifuged at 15 000 rpm for 60 min to remove PVP and all by-products in the supernatant. The precipitates were collected and then re-dispersed in 1.5 mL ethanol. It was centrifuged at 15 000 rpm for 30 min. This procedure was repeated three times. For TEM and TEM–EDS observations, samples were prepared by dropping colloidal solutions of the products onto Cu grids.

3. Analytical instruments

TEM and TEM–EDS images were measured at 200 kV (JEM-2100F ; JEOL). High-resolution (HR)-TEM images of Pd–Ag cubes were measured at 200 kV using spherical aberration corrected scanning (SACS) type TEM (JEM-ARM200M(URP) ; JEOL). XRD patterns of Pd alloys were measured (RINT-TTR Ⅲ with Cu Kα radiation operating at 50 kV and 300 mA; Rigaku). Extinction spectra of the product solutions were measured in the 200–1050 nm region using a spectrometer with CCD (USB4000-XR1 equipped with a CUV–UV cuvette holder; BAS Inc.). Time resolution was either 0.5 or 1.0 s in the present experiments. When time-dependent SPR bands were measured, spectra in a standard quartz cell were measured under continuous stirring of reagent solution.

4. Figs. S1–S6

(a) Pd cubes



(b) Ag nanospheres

(c) Ag nanoprisms

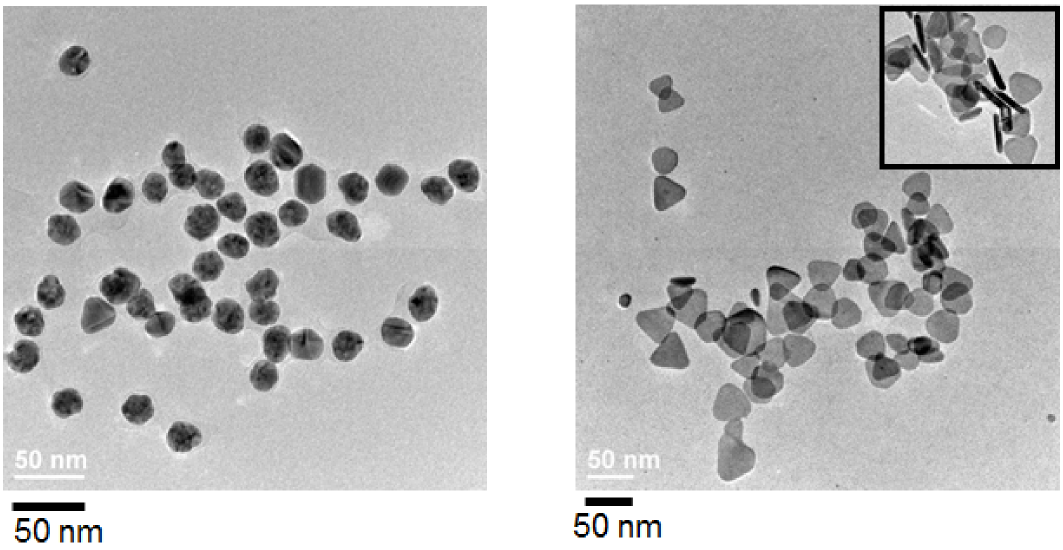


Fig S1. TEM images of (a) Pd cubes, (b) Ag nanospheres, and (c) Ag nanoprisms used for spontaneous alloying experiments before mixing.

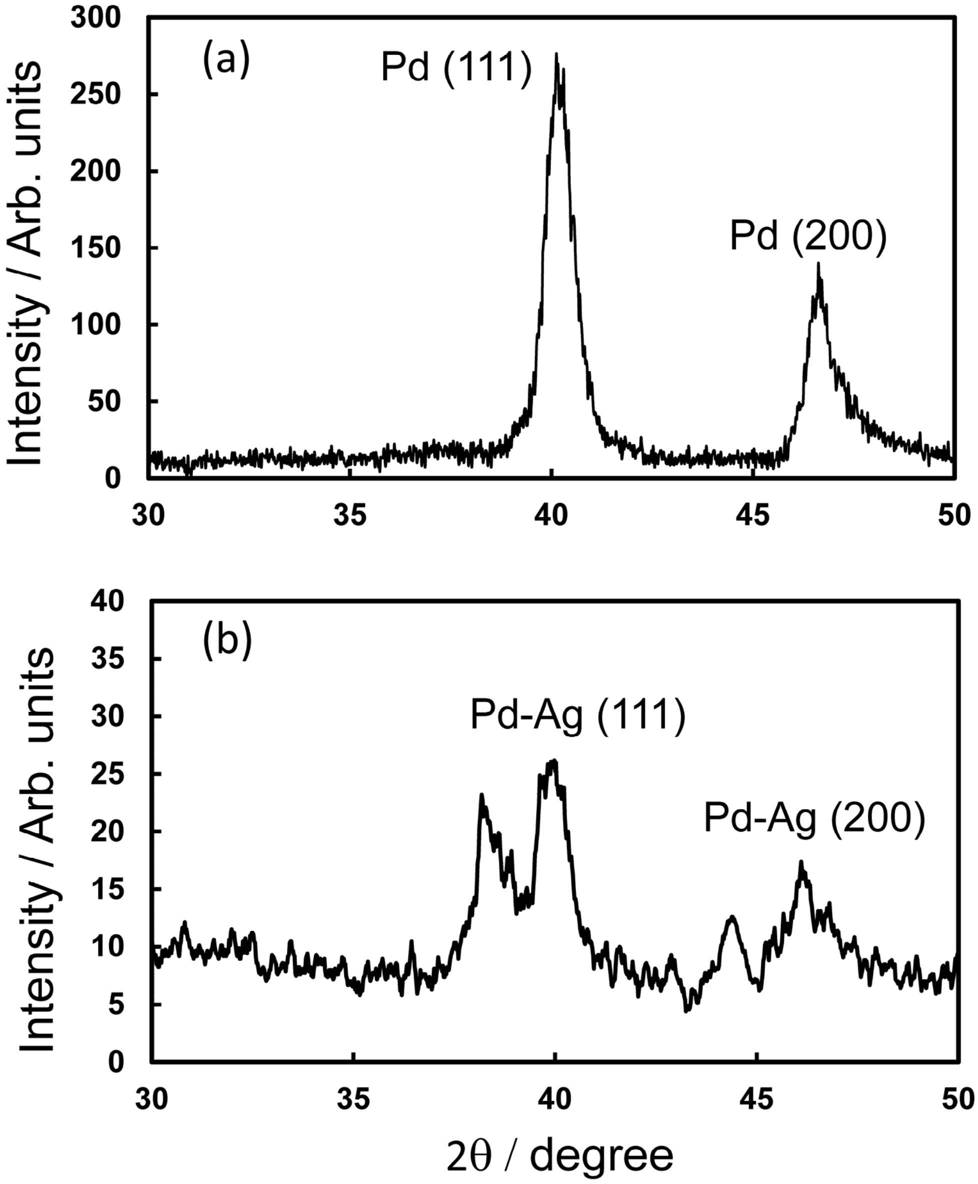


Fig S2. XRD pattern of (a) pure Pd and (b) Pd–Ag alloy cubes prepared from Pd cubes and Ag nanospheres in an aqueous solution at Pd : Ag molar ratio of 75 : 25.

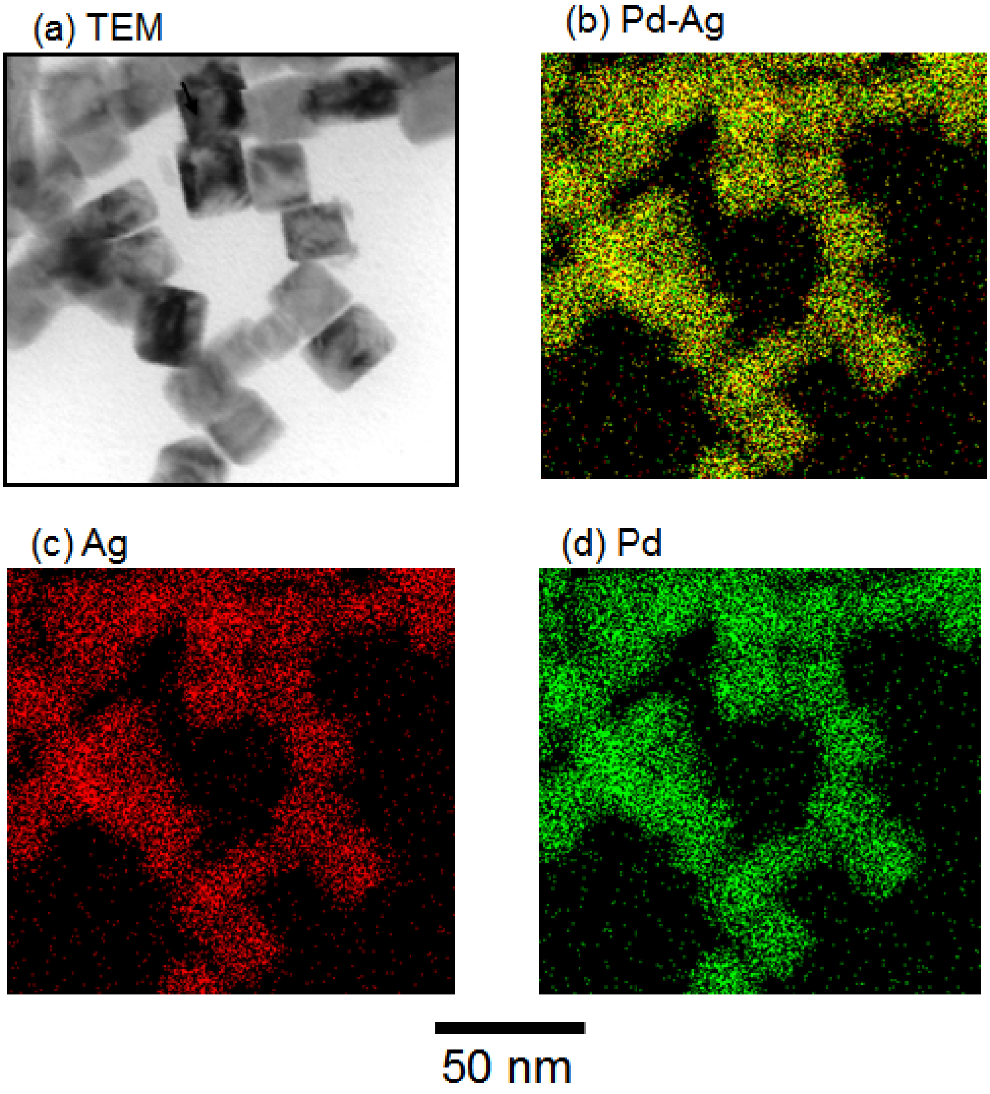


Fig S3. (a) TEM and (b)-(d) TEM–EDS data of products after mixing Pd cubes and Ag nanospheres in an aqueous solution at Pd : Ag molar ratio of 78 : 22.

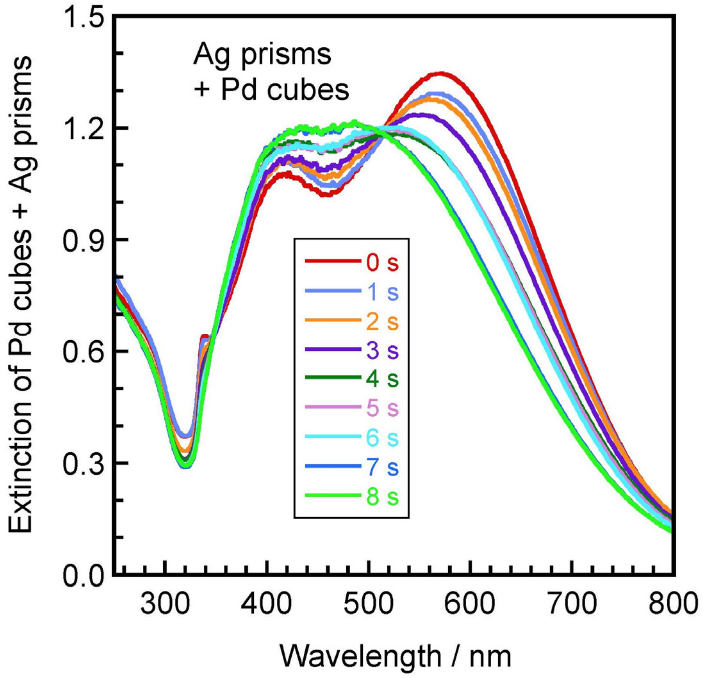


Fig S4. Time evolution of UV–Vis spectra of products observed after mixing Pd cubes and Ag prisms in an aqueous solution at Pd : Ag molar ratio of 0.1 : 1.

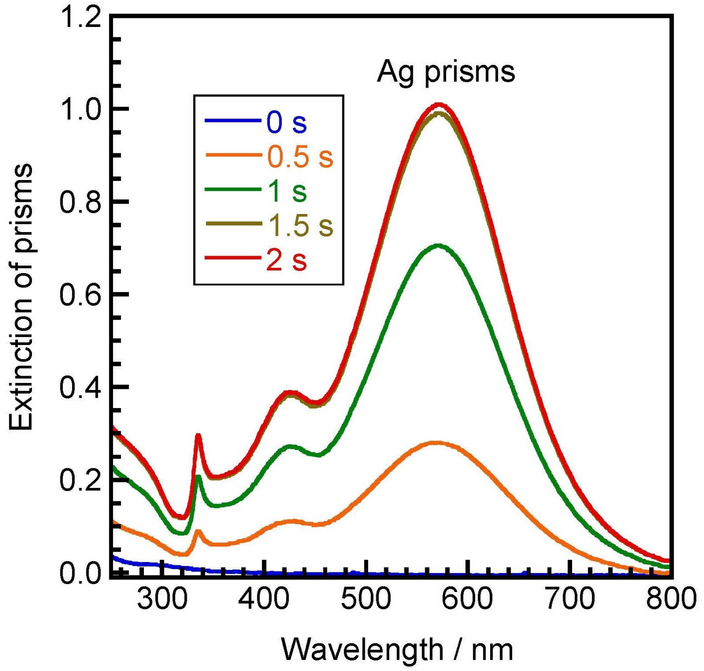


Fig S5. Time evolution of UV–Vis spectra observed after injection of Ag prisms to an aqueous solution.

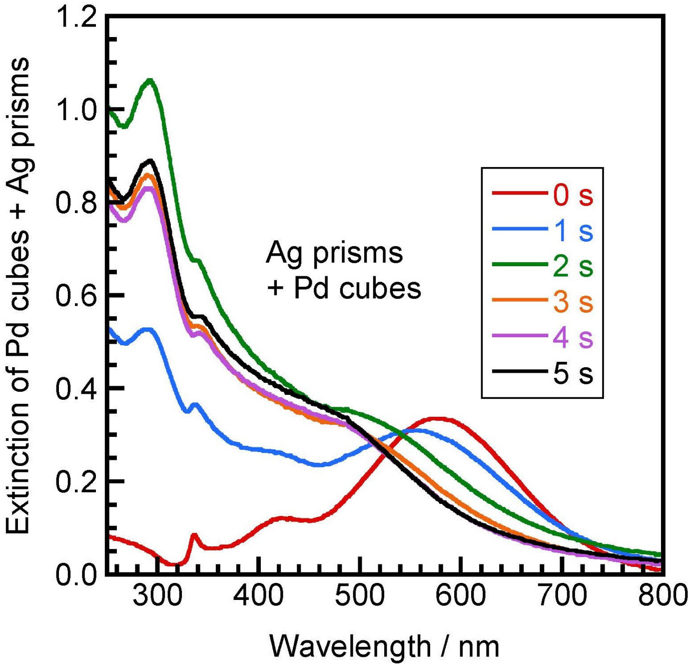
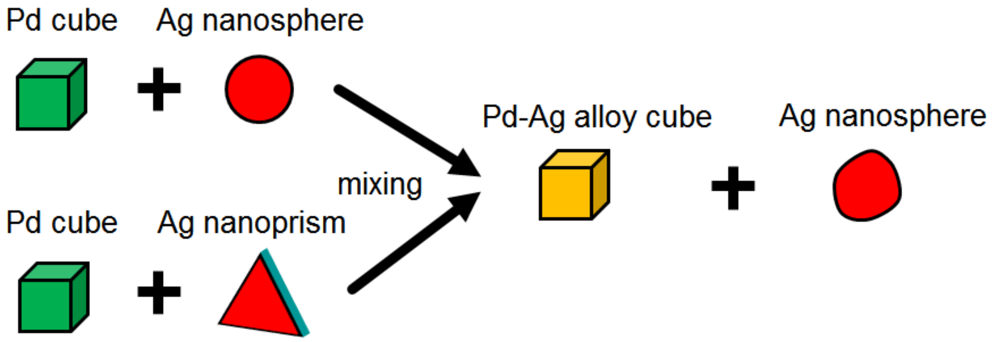


Fig S6. Time evolution of UV–Vis spectra of products observed after mixing Pd cubes and Ag prisms in an aqueous solution at Pd : Ag molar ratio of 78 : 22.

5. Scheme S1



Scheme S1. Spontaneous alloying between Pd cubes and Ag nanostructures at room temperature.

6. References

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2 X. L. Tang, M. Tsuji, M. Nishio and P. Jiang, *Bull. Chem. Soc. Jpn.*, 2009, **82**, 1304.

3 M. Tsuji, S. Gomi, Y. Maeda, M. Matsunaga, S. Hikino, K. Uto, T. Tsuji and H. Kawazumi, *Langmuir*, 2012, **28**, 8845.

7. Acknowledgement

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