

1 Room-temperature Flow Synthesis of Pd–Ru Solid-
2 solution Alloy Nanoparticles Using Microreactor
3 and Catalytic Performance of Carbon Monoxide
4 Oxidation

5 *Shotaro Danjo^a, Hiroto Yoshida^a, Shotaro Hiraide^{a,b}, and Satoshi Watanabe^{a*}*

6 ^aDepartment of Chemical Engineering, Kyoto University, Katsura, Nishikyo, Kyoto 615-8510,
7 Japan

8 ^bInstitute for Aqua Regeneration, Shinshu University, 4-17-1 Wakasato, Nagano 380-8553,
9 Japan

10 *Email: nabe@cheme.kyoto-u.ac.jp

ABSTRACT: The electronic states of solid-solution alloys can be regulated by tuning their composition, thereby affecting their physical and chemical properties. Through nanosizing, solid solution formation can be achieved even for immiscible elements, but conventional synthesis of such alloy nanoparticles (ANPs) often requires harsh conditions, such as high temperature, pressure, and organic solvents. Therefore, developing simpler, low-temperature, liquid-phase synthesis methods is highly desirable. However, reactant diffusion during insufficient mixing of precursor solutions hinders uniform nucleation and composition control. In this study, we synthesized Pd–Ru ANPs in an aqueous solution at room temperature using a microreactor with excellent mixing performance, which created a uniform reaction field. This technique allowed the simultaneous reduction of different ions before nucleation, enabling precise composition control. The resulting Pd–Ru ANPs exhibited uniform size and composition, and their catalytic properties showed enhanced activity compared to monometallic nanoparticles, as evaluated via carbon monoxide (CO) oxidation rate measurements. Notably, under room-temperature conditions, increasing Ru content resulted in a reduced crystallinity and induced localized structural disorder. This unique structural feature enabled optimal CO oxidation activity at a lower Pd composition than that reported previously. This method provides a simple and effective approach for the synthesis of ANPs with controlled compositions under mild conditions.

INTRODUCTION

The growing scarcity of critical elements, such as precious metals, necessitates their optimized usage and alternative strategies for resource conservation and the development of substitutes with comparable or superior functionalities¹⁻⁴. Given these challenges, solid-solution alloys are vital for realizing a sustainable society⁵, as they enable tailored mechanical⁶⁻⁸ and magnetic⁹⁻¹¹ properties that often surpass those of monometallic systems through precise control of elemental compositions, thereby significantly reducing reliance on resources. Moreover, at the nanometer scale, alloy nanoparticles (ANPs) exhibit dramatically enhanced surface-to-volume ratios, facilitating the fine-tuning of electronic structures for superior catalytic activity¹²⁻¹⁸ and improved selectivity^{14,19}, while also enabling unique optical^{20,21} and magnetic²² properties unachievable in bulk alloys. This precise atomic-level mixing affords synergistic effects between constituent elements, yielding superior performance while minimizing the use of scarce metals.

Recent advances in nanotechnology have revealed that combinations of elements previously considered immiscible can form ANPs when the particle size is restricted to the nanometer scale. While top-down approaches that rely on mechanical²³, thermal¹⁴, and laser²⁴ techniques are simple and robust, they face an inherent limitation because precursor bulk alloys follow typical phase diagrams, thus hindering the formation of solid solutions among immiscible elements. In contrast, bottom-up methods, involving the formation of nanoparticles by assembling atoms and molecules in gas-²⁵ or liquid-phase²⁶ media, effectively promote the mixing of such immiscible elements. In fact, Ag–Rh²⁷ and Pd–Ru¹² ANPs have been synthesized via chemical reduction methods such as the polyol method. Notably, despite Ag and Rh lacking intrinsic hydrogen-storage capabilities, Ag–Rh ANPs absorbed hydrogen at approximately half the efficiency of bulk Pd, which is located between Ag and Rh in the periodic table²⁷. Furthermore, Pd–Ru ANPs

exhibited superior catalytic activity in carbon monoxide (CO) oxidation^{12,16} and nitrogen oxide (NO_x) reduction¹³ compared to Rh. In addition, high-entropy ANPs incorporating eight elements into a single nanoparticle were synthesized via a carbothermal shock method at approximately 2000 K, achieving nearly 100% ammonia oxidation conversion and >99% NO_x selectivity¹⁴. Collectively, these studies have highlighted the transformative impact of nanoscale solid-solution alloys on resource management and material innovation.

Building upon the success of the polyol method by Kusada et al., mainstream synthetic methods for ANPs derived from bulk-immiscible systems typically require harsh conditions^{12,14,27,28}, such as high temperature, high pressure, organic solvents, or complicated procedures^{29,30}, to overcome elemental immiscibility. However, for industrial applications, synthesis under aqueous and room-temperature conditions is clearly preferable due to lower energy requirements and reduced environmental impact. For example, Essinger-Hileman et al. demonstrated the successful synthesis of ANPs from bulk-immiscible systems such as Au–Rh, Au–Pt, Pt–Rh, and Pd–Rh in room-temperature aqueous media using sodium borohydride (NaBH₄)³¹; the strong reducing power of NaBH₄ overcame kinetic differences in metal ion reduction. In contrast, despite similar attempts utilizing NaBH₄ under varying temperature and pH conditions, previous studies on Pd–Ru ANPs synthesized in aqueous solutions either showed significant deviations from targeted compositions or failed to form uniform solid-solution alloys, instead yielding separate metallic Pd and amorphous Ru phases or aggregated particles^{32–34}. This limitation underscores the urgent need for improved synthesis strategies, as overcoming it is essential to realizing the full potential of Pd–Ru ANPs for advanced applications. Ideally, if atoms are homogeneously mixed in a supersaturated solution, they should naturally form alloys via instantaneous nucleation. In fact, in the Au–Rh system, Chen et al. reported that when

particle sizes fall below 2 nm, the miscibility of the elements increases across the entire composition range³⁵, while density functional theory (DFT) calculations for the Pd–Ru system by Nanba and Koyama showed that at sufficiently small particle sizes, the free energy of the solid-solution state is lower than that of the phase-separated state³⁶. These experimental and theoretical insights suggest that uniform alloy nuclei can form if solutions are intensely mixed to establish a homogeneous reaction field, and if the reduction reactions proceed so rapidly that differences in reduction kinetics among the metal ions become effectively negligible. Therefore, it is crucial to satisfy the following two conditions:

(1) A strong reductant (e. g. NaBH_4) must be used in sufficiently high concentrations. This condition ensures a uniformly high supersaturation of metal atoms, enabling instantaneous nucleation and minimizing compositional deviations due to differences in reduction kinetics.

(2) Intensive and rapid mixing conditions must be maintained throughout the reaction. This condition establishes homogeneous reaction environment, preventing local concentration gradients and facilitating uniform distribution of metal atoms within the reaction field.

If these criteria are met, the formation of a solid solution and the precise control over the Pd–Ru composition should be attainable under aqueous and room-temperature conditions.

In this study, we realized such a high-intensity mixing environment using a central collision-type microreactor (Figure 1a–b)³⁷, which can achieve complete mixing within several milliseconds^{38,39}. Additionally, this microreactor is designed as a flow system, enabling the continuous synthesis of ANPs. This device has enabled the synthesis of Pt NPs³⁹ and Ni NPs⁴⁰ with a narrow size distribution, Co–Pt ANPs⁴⁰, silica-metal core-shell particles^{41,42}, and metal-organic frameworks^{43,44} through precise control of reaction time. These successful syntheses demonstrate that the excellent mixing performance of the microreactor enables instantaneous

delivery of highly concentrated reducing agents to metal ions, highlighting its suitability for synthesizing bulk-immiscible ANPs. Herein, we demonstrated that microreactor-based synthesis can achieve the formation of bulk-immiscible Pd–Ru ANPs under mild, aqueous, and room-temperature conditions. The microreactor allowed us to eliminate mixing inhomogeneities during nucleation, thereby enabling a focus solely on intrinsic reaction kinetics without the complications caused by nonuniform mixing. By examining various reaction conditions, we clarified the formation mechanism of the ANPs. Finally, the synthesized Pd–Ru ANPs supported on γ -Al₂O₃ were evaluated for catalytic activity via CO oxidation, confirming that our microreactor-based approach yields well-defined, bulk-immiscible ANPs at room temperature. These findings indicate that our microreactor-based synthesis not only facilitates the solid-solution formation of bulk-immiscible elements but also represents a promising platform for advancing heterogeneous catalysis and broader industrial applications.

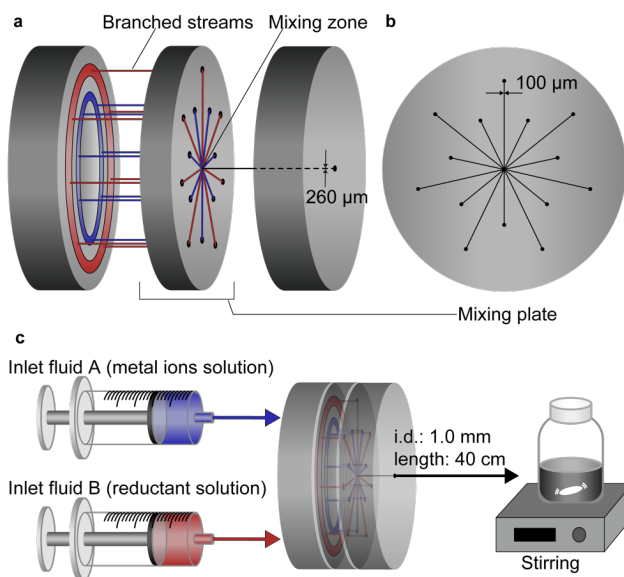


Figure 1. (a) Schematic illustration of the microreactor comprising three plates. (b) Detailed view of the mixing plate within the microreactor. (c) Flow-based synthesis setup of Pd–Ru ANPs

utilizing the microreactor, illustrating separate introduction and rapid mixing of precursor and reducing agent solutions.

EXPERIMENTAL SECTION

Chemicals

Potassium tetrachloropalladate (II) (K_2PdCl_4 , >95.0% purity) was purchased from Kanto Chemical Co., Inc. (Japan). Ruthenium (III) chloride hydrate ($\text{RuCl}_3 \cdot n\text{H}_2\text{O}$, 99.9%), polyvinylpyrrolidone (PVP, molecular weights (MWs) = 1,300,000, 360,000, 40,000, and 10,000), sodium borohydride (NaBH_4 , 99%), poly(acrylic acid) (PAA, MW = 250,000) and poly(sodium 4-styrenesulfonate) (PNaStS, MW = 70,000) were purchased from Merck KGaA (Germany). $\gamma\text{-Al}_2\text{O}_3$ powder was purchased from FUJIFILM Wako Pure Chemical Corporation (Japan). All chemicals were used without further purification. Aqueous solutions of the desired concentrations were prepared by dissolving the original chemicals in ultrapure water (resistivity >18 M Ω ·cm) using an Arium mini system (Sartorius AG, Germany).

Synthesis of Pd–Ru alloy nanoparticles

Pd–Ru ANPs were synthesized via a liquid-phase reduction method using a central collision-type microreactor. The microreactor (Figure 1a) divides inlet fluids A and B into seven microchannels, each with a width of 100 μm , and has a mechanism to collide them from all directions (Figure 1b). The width of the collision area and the post-collision flow path were 260 μm . This type of mixer has an extremely short mixing time of 10^{-4} – 10^{-3} s, as determined by the Villermoux–Dushman method,^{45,46} and exhibits excellent mixing performance compared to conventional

batch-type mixing methods, which have a longer mixing time of 10^{-2} – 10^{-1} s³⁸. An aqueous solution containing Pd^{2+} and Ru^{3+} ions, along with PVP, was prepared as inlet fluid A, and an aqueous NaBH_4 solution was prepared as inlet fluid B. They were loaded into syringes and delivered at an equal volumetric flow rate of 10 mL min^{-1} each using Nexus 6000 syringe pumps (Chemyx Inc., USA) to the microreactor for mixing at room temperature (Figure 1c). The mixed solution was collected in a beaker from the reactor's outlet, which was connected to a PTFE tube (inner diameter of 1.0 mm, length of 40 cm) and continuously stirred at room temperature using a PTFE magnetic stir bar (10 mm in length and 4 mm in diameter) for at least 15 min. Here, pre-mixing concentration was set as a typical condition for the reducing agent: $[\text{Pd}^{2+}] = 4x \text{ mM}$, $[\text{Ru}^{3+}] = 4(1-x) \text{ mM}$, and $[\text{PVP (MW = 1,300,000)}] = 8 \text{ mM}$ (monomer-based) and $[\text{NaBH}_4] = 84 \text{ mM}$ ($x = 0$ – 0.9) and 42 mM ($x = 1$), where x represents the Pd molar fraction and $1-x$ represents the Ru molar fraction in the precursor solution, defined as

$$x = \frac{C_{\text{Pd}}}{C_{\text{Pd}} + C_{\text{Ru}}}, \quad (1)$$

where C_{Pd} and C_{Ru} [mol L^{-1}] are the molar concentrations of Pd^{2+} and Ru^{3+} in the precursor solution, respectively. To evaluate the robustness and reproducibility of the synthetic method, additional experiments were conducted by varying total metal concentrations ($[\text{Pd}^{2+}] = [\text{Ru}^{3+}] = 1$ – 10 mM), while maintaining $[\text{NaBH}_4] = 84 \text{ mM}$ and the molar ratio $([\text{Pd}^{2+}] + [\text{Ru}^{3+}]) / [\text{PVP}] = 0.25$. The synthetic procedure was identical to the typical condition described above. For low-concentration conditions, only $[\text{NaBH}_4]$ was changed to 6 mM , and the same method was employed for the synthesis. When the PVP of other MWs, PAA, and PNaStS were used, solution concentrations were adjusted based on the monomer units, and the same method was employed for synthesis. These concentration conditions are listed in Table S1–3.

Electron microscopy measurements

The NP suspension was diluted tenfold with ultrapure water and drop-cast onto a TEM grid (NP-C15, microgrid pitch: 150 μm ; Oken Trading Co., Ltd.). The grids were then dried overnight at room temperature. Transmission electron microscopy (TEM), annular dark-field scanning TEM (ADF-STEM), and high-angle annular dark-field STEM (HAADF-STEM) images and electron diffraction patterns were acquired using a JEM-2100F (JEOL Ltd., Japan) instrument equipped with a field-emission electron gun at an accelerating voltage of 200 kV. STEM energy-dispersive X-ray spectroscopy (STEM-EDX) analysis was performed for elemental mapping and quantification using the standard simplified quantification method provided by JEM-2100F instrument software. Atomic-resolution HAADF-STEM images were obtained using a JEM-ARM200F (JEOL Ltd., Japan). The particle size distributions from the TEM images (140–570 particles) were determined using ImageJ software⁴⁷.

Energy dispersive X-ray fluorescence spectroscopy

Energy-dispersive X-ray fluorescence spectroscopy (EDXRF) was conducted on the solid samples using an Epsilon 1 instrument (Malvern Panalytical Ltd., UK) for macroscopic elemental composition analysis. A quantitative analysis was performed using external calibration curves (Figure S1). The linearity of the calibration curves for Pd and Ru was verified by measuring the precursor ions and 3 mL of an aqueous PVP solution in a specialized holder at various concentrations. First, 3 mL of the sample solution containing the dispersed NPs were placed in a holder, followed by quantitative analysis to determine the concentration of the target element in the suspension $y_{i,\text{suspension}}$, where i represents elemental species of Pd and Ru. Subsequently, the sample solution was centrifuged at 15,000 rpm, and 3 mL of the supernatant

was placed in another holder for further quantitative analysis to determine $y_{i,\text{centrifuged}}$. The macroscopic elemental composition, $y_{i,\text{solid}}$, of the solid powder was calculated using the following equation:

$$y_{i,\text{solid}} = y_{i,\text{suspension}} - y_{i,\text{centrifuged}}. \quad (2)$$

Synchrotron powder X-ray diffraction measurement and Rietveld refinement

The nanoparticle dispersion was centrifuged at 15,000 rpm after synthesis. After removing the aqueous solution from the supernatant, ultrapure water was added dropwise and subjected to ultrasonic washing before centrifugation at the same speed. After removing water, the samples were dried under vacuum. The powdered samples were ground using an agate mortar and packed into a borosilicate glass capillary with an outer diameter of 0.5 mm (Hilgenberg GmbH, Germany). Synchrotron PXRD measurements were performed at the BL02B2⁴⁸ and BL13XU⁴⁹ beamlines of SPring-8 with exposure times of 30 and 10 s, respectively. During measurements, the capillary was left unsealed and exposed to the atmosphere. *In situ* temperature-rise PXRD measurements were performed at the BL13XU beamline of SPring-8. Heating was achieved by blowing nitrogen through a temperature-controlled gas-handling system installed in the beamline, thereby raising the temperature from room temperature to 450 °C.

Rietveld refinement was performed using RIETAN-FP software⁵⁰. The split pseudo-Voigt function proposed by Toraya⁵¹ was used as the profile function. The calibrated wavelength and zero-shift parameter were obtained via Rietveld refinement of the CeO₂ standard (NIST Standard Reference Material 674a). The crystallite size was calculated using the Halder–Wagner method^{52,53} as follows.

$$\left(\frac{\beta}{\tan\theta}\right)^2 = \frac{K\lambda}{D} \frac{\beta}{\tan\theta \sin\theta} + 16\varepsilon^2, \quad (3)$$

where β is the integral breadth (integrated intensity/peak intensity), θ is the diffraction angle, K is the shape factor, λ is the wavelength, D is the crystallite size, and ε is the micro-strain. The crystallite size calculated is the volume-weighted average size, with $K = 4/3$. To remove the contribution of profile broadening from the optical system and instrument, the sample broadening, β_{sample} , was determined using

$$\beta_{\text{sample}}^2 = \beta_{\text{obs}}^2 - \beta_{\text{instrument}}^2, \quad (4)$$

where β_{obs} is the observed integral breadth and $\beta_{\text{instrument}}$ is the integral breadth of the CeO_2 standard.

Preparation and characterization of catalysts

Pd-Ru ($x = 0, 0.25, 0.5, 0.75, 1$; x represents the proportion of Pd in the precursor mixture) NPs synthesized in the microreactor were supported on $\gamma\text{-Al}_2\text{O}_3$ and prepared by wet impregnation. The $\gamma\text{-Al}_2\text{O}_3$ support was calcined at 800 °C for 5 h at ambient pressure. The volume of the NP suspension was determined such that the precursor ion concentration before synthesis was 1 wt% relative to $\gamma\text{-Al}_2\text{O}_3$. Subsequently, the suspension was mixed with $\gamma\text{-Al}_2\text{O}_3$ powder. The mixture was magnetically stirred at 1,500 rpm at room temperature for 12 h. After stirring, evaporation was performed using a rotary evaporator at 80 °C, followed by vacuum drying at 120 °C for 8 h. The dried powder was pelletized at 3 MPa for 5 min, crushed, and sieved to obtain a grain size of 180–250 μm . The sizes of the as-synthesized Pd-Ru ANPs were determined by TEM (JEM-2100F, accelerating voltage: 200 kV). The supported state of the NPs was examined by HAADF-STEM (JEM-2100F, accelerating voltage: 200 kV) and STEM-EDX. The actual loading of the NPs on $\gamma\text{-Al}_2\text{O}_3$ was determined using Epsilon1 with external calibration curves (Figure S2).

Catalytic test of CO oxidation

Each catalyst (240 mg) was loaded into a tubular quartz reactor (inner diameter: 4 mm) containing quartz wool. To ensure consistency in the surface oxidation state, a feed gas mixture of H₂/Ar (5/95 mL min⁻¹ at 20 °C and 1 atm) was introduced into the catalyst at 100 °C for 30 min at 1 atm. Subsequently, a feed gas mixture of N₂/O₂/CO (98.4, 0.8/0.8 mL min⁻¹ at 20 °C and 1 atm) was introduced over the catalysts at 100 °C for 15 min. The temperature of the catalyst was increased by 10 °C every 15 min until the reaction reached completion, and the CO concentration in the outlet gas was analyzed using a gas chromatograph (GC; GC-14B, Shimadzu, Japan) equipped with a thermal conductivity detector, as well as PorapakQ 50/80 (2.0 m) and MA-5A 50/80 (3.0 m) columns maintained at a column temperature of 60 °C. The CO conversion at each temperature was calculated as follows:

$$\text{CO conversion} = \frac{C_{\text{CO,in}} - C_{\text{CO,out}}}{C_{\text{CO,in}}}, \quad (5)$$

where $C_{\text{CO,in}}$ and $C_{\text{CO,out}}$ are the concentrations of the feed and effluent gases, respectively, as measured by the GC. The reaction was assumed to be of zero order, and the apparent rate constant was calculated using Eq. (6);

$$k_{\text{eff}} = \frac{\text{CO conversion} \times v_{\text{CO}}}{m_{\text{Pd,Ru}}}, \quad (6)$$

where k_{eff} [mol s⁻¹ mg⁻¹] is the effective CO conversion rate per actual metal loading, v_{CO} [mL s⁻¹] is the molar flow rate, and $m_{\text{Pd,Ru}}$ [mg] is the loading of Pd and Ru on $\gamma\text{-Al}_2\text{O}_3$.

RESULTS AND DISCUSSION

Synthesis of Pd–Ru ANPs at room temperature

Pd–Ru ANPs ($x = 0.5$, where x represents the molar fraction of Pd relative to the total Pd and Ru in the precursor solution) were synthesized at room temperature using a central collision-type microreactor (Figure 1a–c) under a typical concentration set (Table S1). Upon mixing an aqueous solution containing Pd^{2+} , Ru^{3+} , and PVP (MW = 1,300,000) with an aqueous NaBH_4 solution in the microreactor, the mixed solution immediately turned black (Figure 2a). Transmission electron microscopy (TEM) revealed uniform NPs with an average size of 5.3 ± 1.1 nm (Figure 2b and Figure S3). An atomic-resolution high-angle annular dark-field scanning TEM (HAADF-STEM) image (Figure 2c) and fast Fourier-transform (FFT) image (Figure 2d) of a single particle showed a polycrystalline structure with a face-centered cubic (FCC) phase. The high-resolution TEM image and electron diffraction pattern indicated the presence of multiple crystalline domains within the primary particles, including the FCC phase (Figure S4). This polycrystallinity, which is often observed in the liquid-phase reduction method using NaBH_4 as the reductant⁵⁴, is attributed to the presence of many small nuclei that grow and coalesce into primary particles. STEM energy-dispersive X-ray spectroscopy (STEM-EDX) of a single particle (Figure 2e–g) and its corresponding intensity profile (Figure 2h) demonstrated homogeneous distributions of Pd and Ru within the particle. Similar analyses performed on multiple particles confirmed consistent compositional homogeneity across the nanoparticle ensemble (Figure 2i–j and Figure S5a). Pd compositions measured by STEM-EDX and energy dispersive X-ray fluorescence (EDXRF) were 0.51 ± 0.04 and 0.52 ± 0.01 , respectively, matching the target of 0.50. Hence, the microreactor-based room-temperature synthesis produced Pd–Ru ANPs with highly homogeneous compositions. Synchrotron powder X-ray diffraction

(PXRD) measurements (Figure 2k) revealed a characteristic peak at approximately $2\theta = 5.38^\circ$, not attributable to the bulk Pd (FCC) or Ru (hexagonal close-packed, HCP) phases. A previous report indicated that Pd–Ru ANPs ($x = 0.5$) have both FCC and HCP structures¹². The ANPs synthesized in this study were expected to have both phases. Double-phase Rietveld refinement provided lattice constants of $a_{\text{fcc}} = 3.85 \text{ \AA}$ for the FCC phase and $a_{\text{hcp}} = 2.77 \text{ \AA}$, $c_{\text{hcp}} = 4.45 \text{ \AA}$ for the HCP phase. These refined values are smaller than the FCC constant of Pd NPs ($x = 1$), $a_{\text{fcc}} = 3.91 \text{ \AA}$, but larger than the HCP constants of Ru NPs ($x = 0$), $a_{\text{hcp}} = 2.72 \text{ \AA}$ and $c_{\text{hcp}} = 4.40 \text{ \AA}$. Since Pd's atomic radius ($1.37 \text{ \AA}$) exceeds Ru's ($1.33 \text{ \AA}$), the results indicate well-mixed substitutional solid solutions: Ru in the Pd-derived FCC lattice and Pd in the Ru-derived HCP lattice.

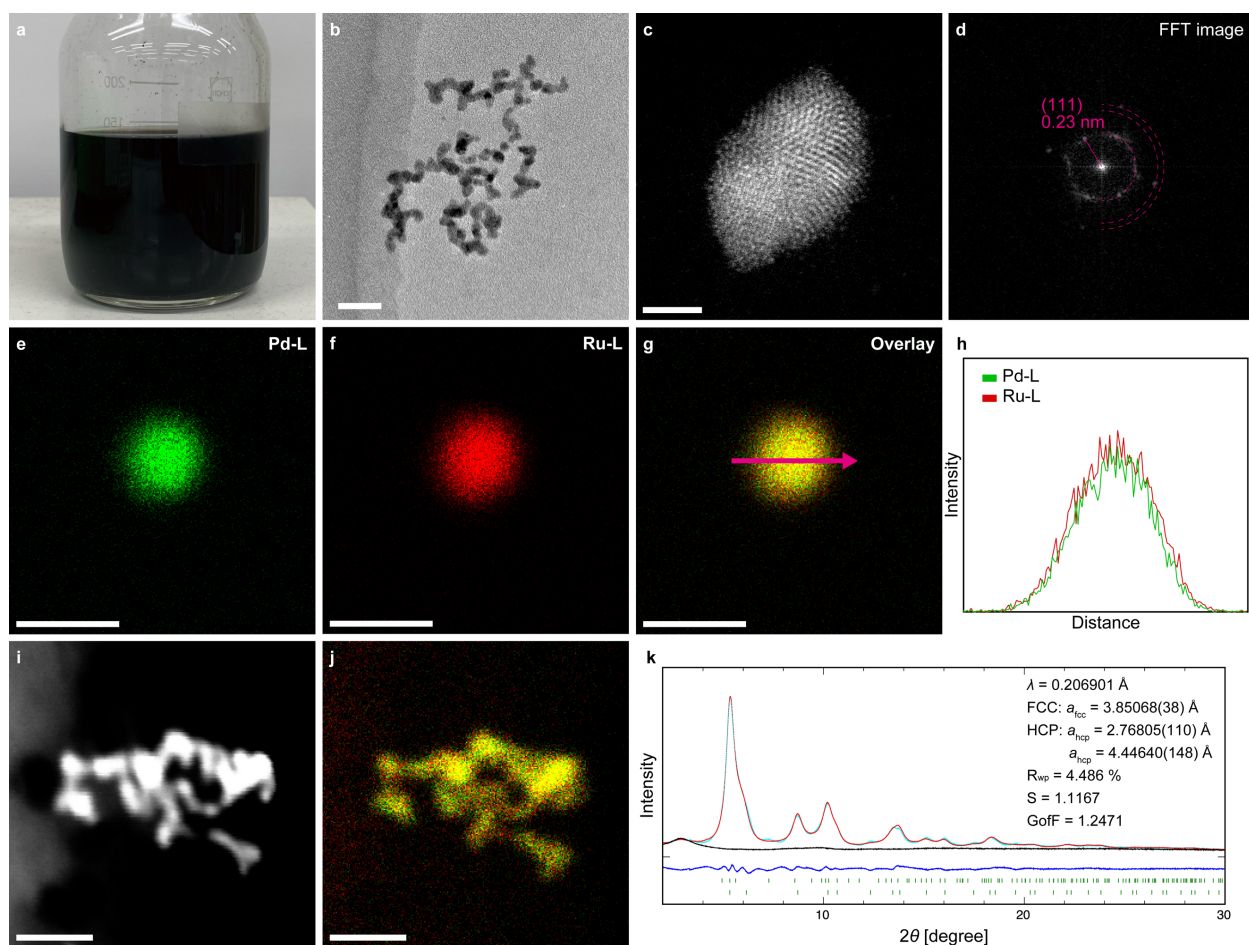


Figure 2. (a) Photograph of Pd–Ru ANP suspension ($x = 0.5$) six months after synthesis. (b) TEM image of Pd–Ru ANPs. (c) Atomic-resolution HAADF-STEM image of a single Pd–Ru ANP. (d) Corresponding FFT pattern derived from (c). STEM-EDX elemental maps showing the spatial distributions of (e) Pd (green), (f) Ru (red), and (g) their overlay. (h) STEM-EDX line-scan analysis of Pd-L (green) and Ru-L (red) intensities along the arrow in (g). (i) ADF-STEM image of Pd–Ru ANPs. (j) Overlay of STEM-EDX elemental maps (Pd-L and Ru-L) corresponding to (i). (k) Synchrotron PXRD pattern of synthesized Pd–Ru ANPs (experimental: red dots; calculated: light blue line). Black and dark blue lines represent the background and difference profiles, respectively. The wavelength is 0.206901 Å. Scale bars are 20 nm in (b), 2 nm in (c), 10 nm in (e–g), and 25 nm in (i–j).

The initial composition was varied from $x = 0$ to 1 under a typical concentration set, and Pd–Ru ANPs were synthesized using the microreactor. TEM showed single-nanometer particles, increasing from 2.7 ± 1.0 nm to 6.7 ± 1.6 nm as x increased (Figure S3). The ADF-STEM images and STEM-EDX elemental maps (Figure S5b–g), along with the overlay images (Figure 3a–f), confirmed the uniform Pd and Ru distributions across the entire composition range, as in the case of $x = 0.5$. Additionally, STEM-EDX and EDXRF analyses revealed that the composition of the synthesized ANPs closely matched that of the initial precursor (Figure 3g). The microreactor's strong mixing enabled room-temperature control of the Pd–Ru ANP composition. PXRD patterns (Figure 3h) indicated a continuous change from Pd NPs ($x = 1$) to Ru NPs ($x = 0$). Lattice constants (Figure 3i) yielded by Rietveld refinement (Figure S6(i)) displayed a linear trend with respect to composition, which adheres to Vegard's law and supports the formation of substitutional solid solutions. The volume-weighted average crystallite sizes

(Figure S6(ii)) were smaller than those in the TEM image (Figure S3), supporting the presence of polycrystalline particles. PXRD patterns indicate that Ru-rich conditions ($x \leq 0.4$) yielded ANPs with relatively low crystallinity. Notably, $\sqrt{2}a_{\text{hcp}}$ exceeded a_{fcc} (Figure 3i), in contrast to earlier findings where $\sqrt{2}a_{\text{hcp}}$ and a_{fcc} were similar¹². This discrepancy in HCP lattice constants suggests structural disorder and/or localized strain in the Ru-rich NPs. *In situ* temperature-rise PXRD measurements revealed that the initial broad peaks sharpened upon heating (Figure S7), indicating that low HCP-phase crystallinity is inherent to the room-temperature synthesis. The structural disorder inherent to this low-temperature route may enhance the surface activity compared to that of more crystalline ANPs, offering potential benefits in catalytic applications.

To confirm reproducibility and robustness of the synthetic approach, additional experiments were conducted under varied metal ion concentrations ($[\text{Pd}^{2+}] = [\text{Ru}^{3+}] = 1\text{--}10\text{ mM}$) while maintaining $[\text{NaBH}_4] = 84\text{ mM}$ and $([\text{Pd}^{2+}] + [\text{Ru}^{3+}]) / [\text{PVP}] = 0.25$. Synchrotron PXRD patterns indicated negligible variations in crystal structures and phase compositions across this concentration range (Figure S8a). Additionally, particle sizes determined by TEM analysis revealed consistent nanoparticle sizes ranging from 5 to 6 nm (Figure S8b), verifying that the synthetic method reliably yields Pd–Ru ANPs with consistent compositional and structural properties.

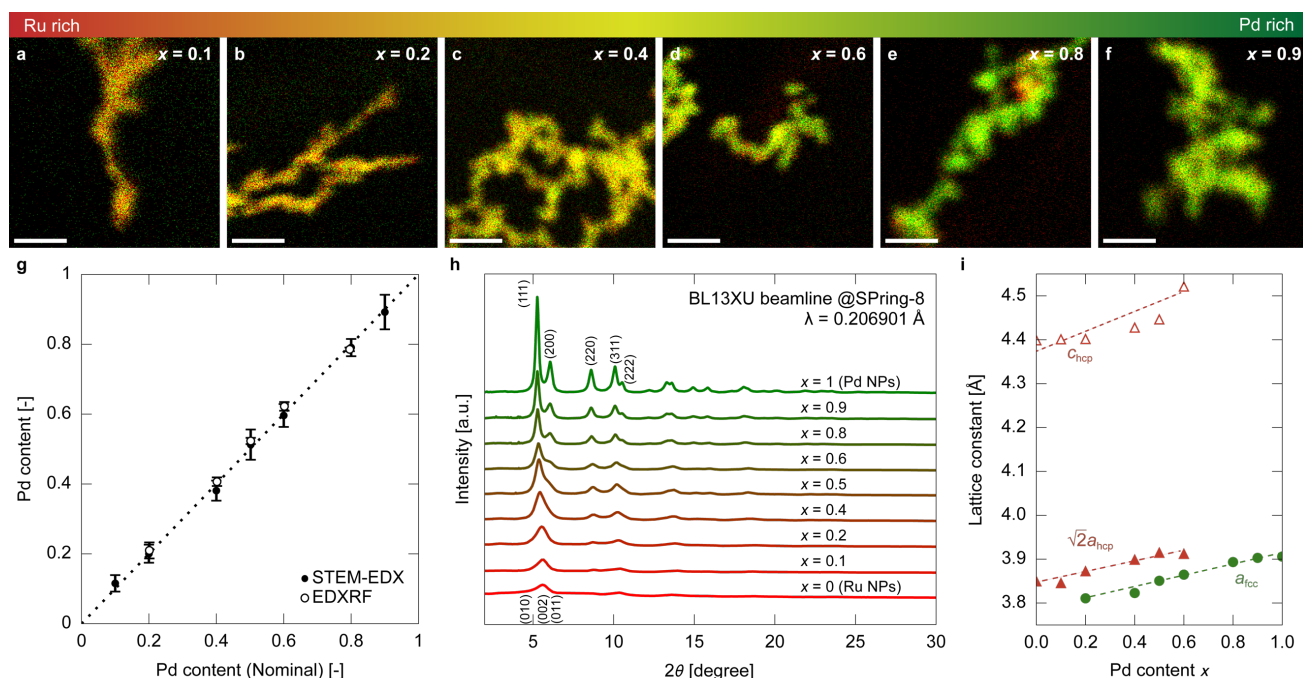


Figure 3. Overlay images of STEM-EDX elemental maps (Pd-L: green, Ru-L: red) for Pd–Ru ANPs synthesized with nominal Pd molar fraction $x =$ (a) 0.1, (b) 0.2, (c) 0.4, (d) 0.6, (e) 0.8, and (f) 0.9. (g) Quantitative compositions determined by STEM-EDX and EDXRF analyses plotted against nominal Pd molar fraction. (h) Synchrotron PXR patterns of Pd–Ru ANPs across the full composition range ($x = 0$ – 1). The wavelength is $0.206901 \text{ \AA}$. (i) Lattice constants of the FCC and HCP phases determined by Rietveld refinement from PXR data. Scale bars are 25 nm in (a–f).

Microreactor vs. conventional batch mixing

To investigate the effects of the mixing modes on the particle formation process, ANPs ($x = 0.5$) were synthesized using reactors with weaker mixing under typical conditions. Different mixing sequences were employed: (a-i) rapid addition of an aqueous precursor solution (solution A) to an aqueous reductant solution (solution B) (Figure 4a), (a-ii) rapid addition of solution B to

solution A, (b-i) rate-controlled addition of solution A to solution B at 5 mL min⁻¹, and (b-ii) rate-controlled addition of solution B to solution A at 5 mL min⁻¹ (Figure 4b). ADF-STEM images of the synthesized particles and STEM-EDX elemental maps (Figure S9), along with their overlay images (Figure 4a(i)–(ii) and Figure 4b(i)–(ii)), revealed that some particles exhibited a compositional bias under batch-type mixing. Moreover, the degree of composition bias became more pronounced when semi-batch-type methods were used. Since the only difference among microreactor-based, batch-type, and semi-batch-type syntheses is the mixing procedure, the initial mixing conditions strongly influence the resulting composition. In a microreactor, metal ions and reductant molecules are rapidly and uniformly dispersed, allowing homogeneous reduction to form alloy nuclei with a uniform composition. These nuclei then collide and coalesce into primary particles (Figure 4c). In contrast, in batch-type mixing with weaker mixing intensity, domains rich in metal ions and reductants form immediately after combining the solutions, causing the reductant to be consumed preferentially by the more easily reducible Pd ions at the boundary regions between domains, thus producing Pd-rich particles first. The Ru ions are then reduced, leading to the formation of Ru-rich particles (Figure 4d). These results highlight the importance of increasing the mixing intensity to enhance collision between reductant molecules and metal ions, which is crucial for controlling final particle composition.

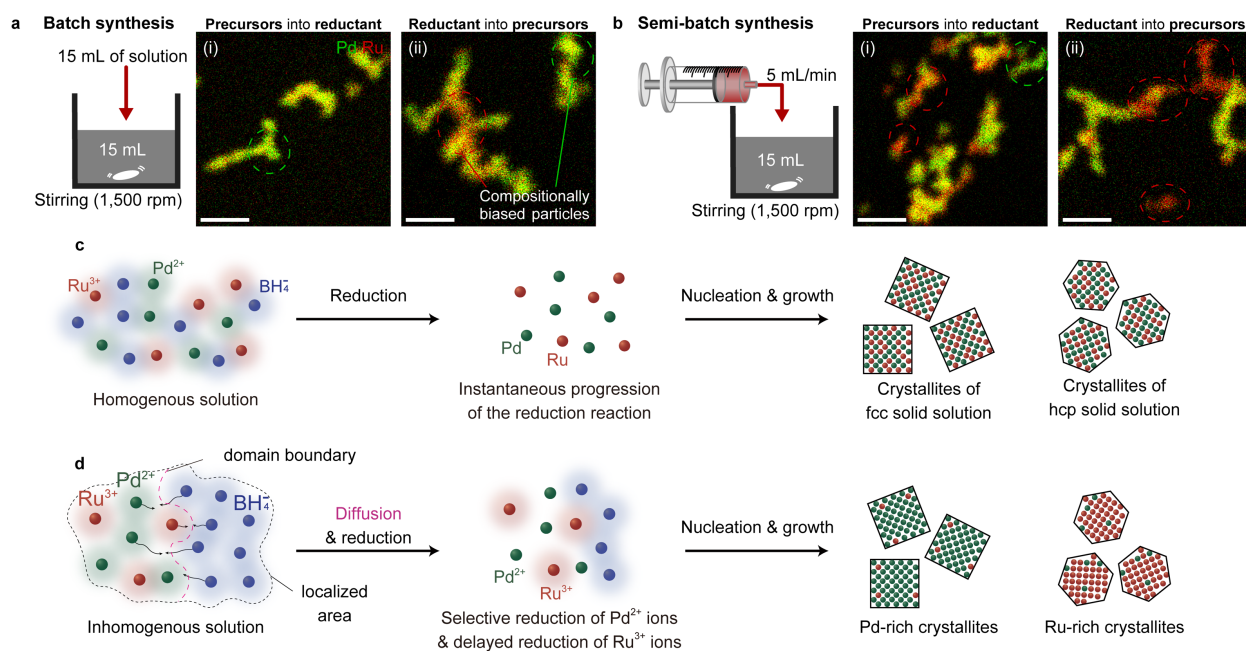


Figure 4. (a) Overlay STEM-EDX elemental maps (Pd-L: green, Ru-L: red) of Pd–Ru ANPs ($x = 0.5$) synthesized by batch-type mixing: rapid addition of (i) precursor into reductant solution and (ii) reductant into precursor solution. (b) Overlay STEM-EDX elemental maps of Pd–Ru ANPs ($x = 0.5$) synthesized by semi-batch-type mixing: controlled addition at 5 mL min^{-1} (i) precursor into reductant and (ii) reductant into precursor. Schematic illustrations comparing nucleation processes under (c) high-intensity mixing (microreactor) and (d) low-intensity mixing (batch and semi-batch mixing). Scale bars are 25 nm in (a(i–ii), b(ii)).

Effect of $[\text{NaBH}_4]$

Typical concentration conditions employed a large excess of NaBH_4 (84 mM) to ensure a rapid precursor reduction and successfully produced Pd–Ru ANPs with arbitrary compositions. To elucidate NaBH_4 's role, Pd–Ru ANPs ($x = 0\text{--}1$) were synthesized using a lower $[\text{NaBH}_4]$ of 6 mM (Table S1). As demonstrated in synchrotron PXRD patterns of the resultant particles (Figure

5a), compared to the typical $[\text{NaBH}_4]$ condition, the FCC (111) reflection shifted to a lower angle at lower $[\text{NaBH}_4]$ (Figure S10). A lower-angle peak shift indicates an increased d-spacing and suppressed dissolution of Ru into the FCC phase. To further quantify the degree of suppressed dissolution, we performed single-phase Rietveld analysis of the FCC phase to refine the lattice constants for $x = 0.4\text{--}1$ (Figure 5b) because the PXRD patterns did not show the HCP phase at low $[\text{NaBH}_4]$. Consequently, the slope of the lattice constant as a function of composition at low $[\text{NaBH}_4]$ was approximately 47% smaller than that under typical $[\text{NaBH}_4]$ conditions, demonstrating the suppressed formation of FCC phase solid solutions despite strong mixing in the microreactor. Moreover, when both the mixing intensity and reductant concentration were low (batch mixing with low $[\text{NaBH}_4]$), increasing the Ru^{3+} ion feed composition barely decreased the lattice constant a_{fcc} (Figure 5b and Figure S11), demonstrating a further suppression of solid-solution formation relative to that observed in microreactor synthesis.

Based on the above results, possible mechanisms for the formation of the solid-solution phase are schematically summarized in Figure 5c–d. In the high-intensity mixing field generated by the microreactor, with a large excess of NaBH_4 as in the typical concentration condition, reduction rates of precursor ions were remarkably high; thus, the nucleation and/or particle growth process was assumed to be the rate-limiting step (Figure 5c). Under these conditions, crystal structures of the particles were thermodynamically controlled. In other words, a rapid reduction reaction leads to the formation of nuclei with a uniform distribution of binary atoms, which corresponds to the most stable state on a single-nanometer scale according to the DFT calculations reported by Nanba and Koyama³⁶, instead of separate Pd and Ru nuclei. In contrast, with a slight excess of NaBH_4 , the reduction rate was inevitably low, as in the low-concentration condition, thereby

386 making this reduction process the rate-limiting step (Figure 5d). Because the reduction of Pd^{2+}
387 ions is faster than that of Ru^{3+} ions based on the redox potential (Pd^{2+}/Pd : 0.95 V vs. standard
388 hydrogen electrode (SHE); Ru^{3+}/Ru : 0.39 V vs. SHE¹⁵), Pd^{2+} ions are preferentially reduced to
389 form nuclei in the FCC phase. In these nuclei, the crystal phase is kinetically selected by
390 elemental components with higher production rates of atoms, as reported by Zhang et al⁵⁵.
391 During the subsequent particle growth process, the reduction of Ru^{3+} ions was incomplete,
392 resulting in the formation of Pd-rich particles. Therefore, increasing the reduction rate in a high-
393 intensity mixing field generated by the microreactor is crucial for the formation of solid-solution
394 ANPs with uniform compositions. Notably, these results clearly demonstrate why previous
395 studies, employing either low concentrations of NaBH_4 or batch mixing with insufficient mixing
396 intensity, were unsuccessful in forming uniform Pd–Ru solid-solution alloys. Thus our
397 hypothesis—that a combination of high concentrated NaBH_4 and intensive mixing conditions is
398 critical for solid-solution alloy formation—is successfully verified by the experimental results
399 demonstrated above.

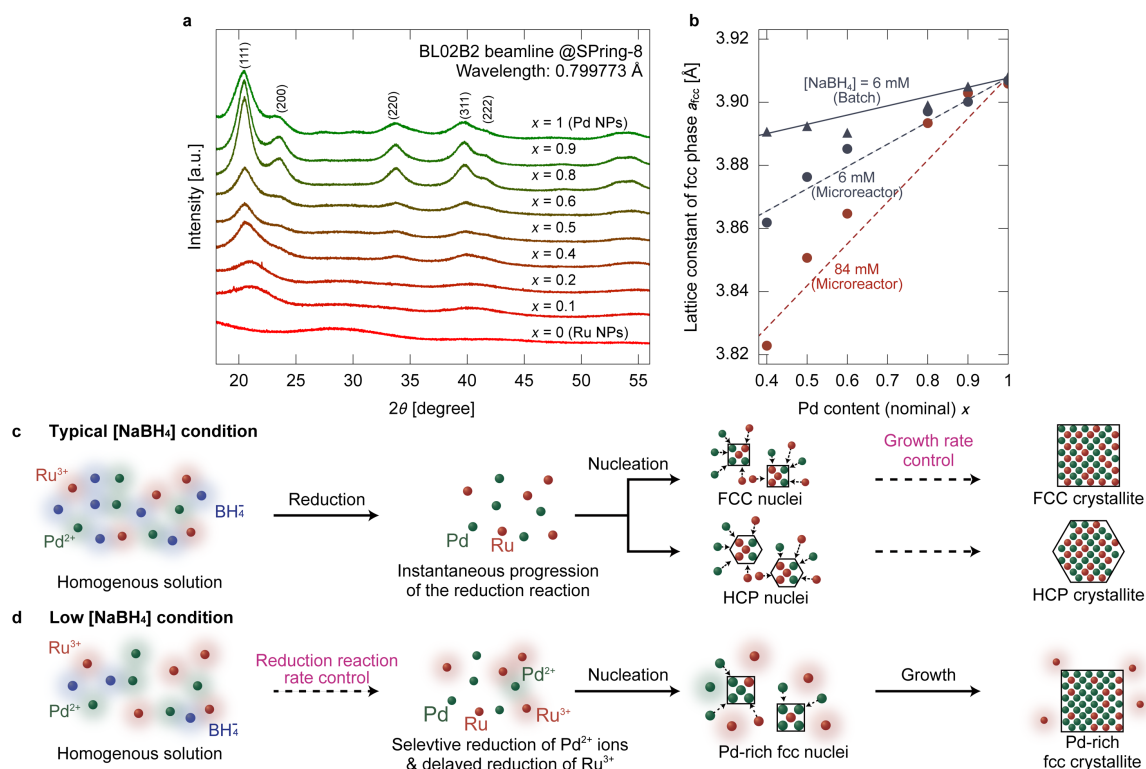


Figure 5. (a) Synchrotron PXRD patterns of Pd–Ru ANPs ($x = 0$ – 1) synthesized at low $[\text{NaBH}_4]$ conditions. The wavelength is $0.799773 \text{ \AA}$. (b) FCC lattice constants of Pd–Ru ANPs synthesized at typical (microreactor, high $[\text{NaBH}_4]$) and low-concentration (microreactor and batch-type mixing, low $[\text{NaBH}_4]$), determined by Rietveld refinement. Schematic models illustrating Pd–Ru ANP formation under microreactor conditions: (c) high reduction rate (typical condition) and (d) low reduction rate (low-concentration condition).

Colloidal stability

After ANP synthesis under typical concentration conditions, the ANP suspension remained stable for over six months (Figure 2a). The synthesized particles exhibited chain-like assemblies (Figure 2b). To investigate the effect of the polymer chain length on the particle formation

process, Pd–Ru ANPs ($x = 0.5$) were synthesized using PVP with MWs of 10,000, 40,000, 360,000, and 1,300,000 at a fixed [PVP] of 40 mM (Table S2). TEM analysis revealed that chain-like assemblies were shorter for PVP with smaller MW (Figure S12), indicating that the ANPs were protected along PVP chains. During the formation process, precursor ions are reduced and nucleated from a rapidly supersaturated solution to form crystallites with a few nanometers in size, which then unite to form primary particles. Subsequently, several PVP molecules adsorbed onto the primary particles to protect them by adsorbing onto their particle surfaces, forming chain-like structures (Figure 6). Notably, larger particles approximately 12 nm in size were observed when using PVP with an MW of 10,000. This results from the aggregation of smaller primary particles because the steric repulsion of the short polymer chains is not strong enough to protect primary particles from aggregation.

The long-term stability of the resultant ANP suspensions demonstrates the excellent particle-protection ability of PVP. Focusing on the electron-donating function and bulkiness of the pyrrolidone groups, control experiments were conducted using PAA or PNaStS at a fixed concentration on a monomer basis as a protective agent instead of PVP (Table S3). PAA possesses electron-donating but less bulky carboxyl groups, whereas PNaStS possesses bulky benzenesulfonic groups that lack electron-donating functions. For both the polymers, synthesis using a microreactor resulted in immediate particle aggregation and precipitation (Figure S13). These results indicate that the combination of electron-donating function and bulkiness is critical for stabilizing ANPs. In this Pd–Ru system, PVP achieves an optimal balance between surface adsorption owing to its electron-donating ability and steric repulsion between particles after adsorption, allowing the colloidal dispersion state to be maintained for an extended period.

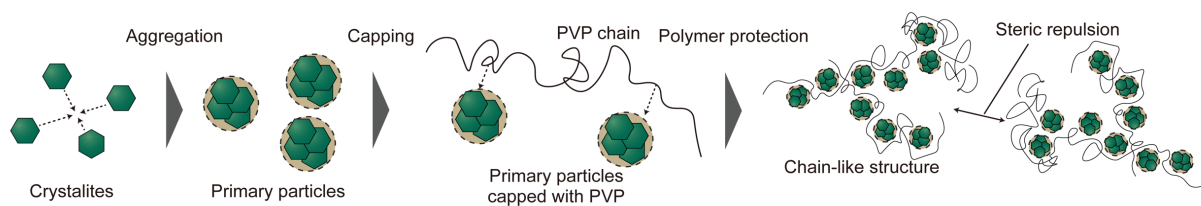


Figure 6. Proposed mechanism illustrating PVP-mediated growth and stabilization of primary ANP crystallites, resulting in chain-like assemblies.

CO oxidation measurement

The crystal structure of ANPs synthesized at room temperature differs from that of particles synthesized at high temperatures, such as via the polyol method, in terms of crystallinity and lattice constant, potentially altering their catalytic performance. Therefore, we evaluated the catalytic performance of the room-temperature-synthesized Pd–Ru ANPs ($x = 0, 0.25, 0.5, 0.75$, and 1) supported on $\gamma\text{-Al}_2\text{O}_3$ by measuring their CO oxidation activity (Figure 7a). HAADF-STEM images (Figure 7b–f) confirmed that ANPs were anchored on $\gamma\text{-Al}_2\text{O}_3$, displaying clear contrast against the support matrix. STEM-EDX elemental maps (Figure S14) further verified the uniform dispersion of NPs supported on $\gamma\text{-Al}_2\text{O}_3$. Size distributions of the as-synthesized particles were obtained from TEM images (Figure S3). As shown in Figure 7g, alloy formation enabled the CO oxidation reaction to proceed even at relatively low temperatures, which is consistent with a previous report¹². Arrhenius plots of the CO oxidation rate per metal loading (Figure 7h) revealed that activation energy decreases linearly from 107 to 70 kJ mol^{-1} as Pd content increases. However, the highest catalytic activity was observed at $x = 0.25$, when the CO oxidation rate per metal loading was the highest at lower temperatures. This trend contrasts with that reported for polyol-synthesized Pd–Ru ANPs¹², which showed optimal performance at $x =$

0.5. Previous studies using X-ray absorption fine structure spectroscopy and hard X-ray photoelectron spectroscopy have shown that the high catalytic activity of the Pd–Ru system arises from a smaller coordination number than that of the bulk crystal and from electronic transitions from Pd to Ru¹⁶. In this study, compositional analysis from STEM-EDX and lattice constant refinements from synchrotron PXRD consistently confirm alloy formation. Moreover, HR-TEM images showed clear lattice fringes across the entire composition range (Figure S4), while PXRD peak intensities gradually weaken and broaden ($x \leq 0.4$, Figure 3h) and the volume-weighted average crystallite size remains below 2.2 nm (Figure S6(ii)) as the Ru content increases, all of which suggest local structural disorder near the surface that is inherent to room-temperature synthesis. We suggest that this unique local disorder, which arises from room-temperature synthesis, contributes to the enhancement of the CO oxidation activity.

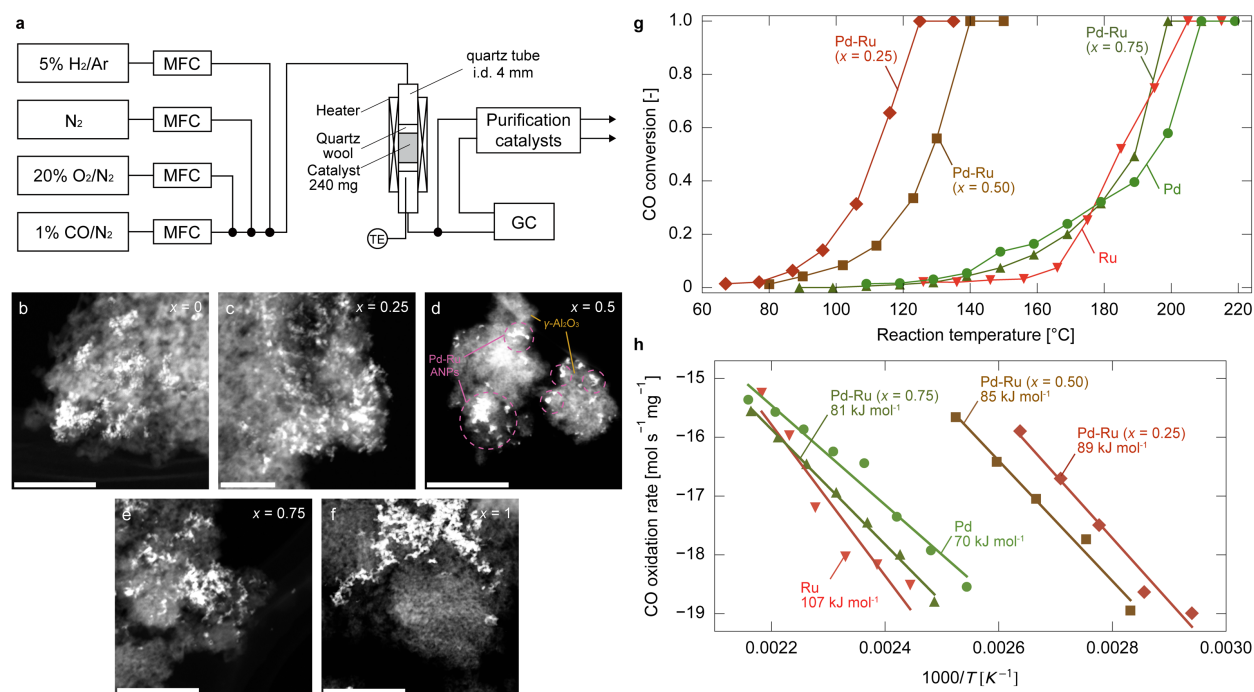


Figure 7. (a) Schematic illustration of the experimental setup used for CO oxidation reaction measurement. b–f, ADF-STEM images of Pd–Ru ANPs synthesized with nominal Pd molar

fractions (x) = (b) 0, (c) 0.25, (d) 0.5, (e) 0.75, and (f) 1 supported on γ -Al₂O₃. (g) CO conversion measured as a function of reaction temperature for supported Pd–Ru ANPs. (h) Arrhenius plots showing CO oxidation reaction rates per metal loading. Scale bars are 100 nm in (b, c, e) and 200 nm in (d, f).

CONCLUSIONS

In this study, Pd–Ru ANPs were successfully synthesized over the entire compositional range at room temperature by controlling the rate-limiting step using a microreactor with an excellent mixing performance, thereby eliminating mixing heterogeneity. The formation of the solid-solution phase was enhanced as the reduction rate increased, and NaBH₄ concentration of 4 mM was found to be sufficient to achieve uniform compositions. The results obtained using PXRD, STEM-EDX, and EDXRF confirmed successful room-temperature composition control. Furthermore, comparisons with batch-type syntheses clearly demonstrated that mixing intensity and homogeneity were crucial for a reproducible ANP composition, as shown by comparisons with weaker batch-type syntheses. Notably, Pd–Ru ANPs with higher Ru composition ($x = 0.75$) demonstrated enhanced CO oxidation performance relative to previously reported values ($x = 0.50$), indicating that the structural disorder associated with reduced crystallinity at high Ru composition enhances CO oxidation activity.

Despite the successful synthesis and enhanced catalytic performance, several limitations remain:

1. Scalability: Although the microreactor demonstrated excellent mixing performance at the laboratory scale, long-term operations may be hindered by potential channel clogging and

limited throughput. Future studies should explore alternative reactor designs and optimize flow conditions to ensure consistent performance at larger production volumes.

2. Generality: This study focuses on the Pd–Ru system. Extending the microreactor-based method to other immiscible or multielement alloys is necessary to evaluate its versatility and identify any system-specific synthesis challenges.

3. Structural Control: The decrease in crystallinity with increasing Ru content improved the CO oxidation activity, but its effects on other catalytic reactions remain unclear. Further investigation into the relationship between nanoparticle structure, crystallinity, and catalytic performance across diverse processes is therefore required.

4. Surface Characterization: Advanced surface analysis methods, such as *in situ* X-ray absorption spectroscopy and CO stripping voltammetry, yield critical insights into the electronic state and chemical environment of alloy surfaces, potentially elucidating correlations with catalytic activity.

Addressing these challenges is essential for advancing ANP synthesis methodologies and their integration into practical catalytic systems, ultimately enabling the development of more efficient and sustainable technologies.

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Supporting Information

Detailed synthesis conditions for Pd–Ru alloy nanoparticles; EDXRF calibration curves and elemental analyses for both suspension and solid-supported samples; TEM images along with particle size distributions; HR-TEM images; electron diffraction patterns; HAADF-STEM images; STEM-EDX elemental maps; Rietveld refinement results of synchrotron PXRD data; in situ temperature-rise synchrotron PXRD measurements; additional synchrotron PXRD and TEM size analyses under varied precursor concentrations, reductant concentrations, and mixing conditions; and colloidal stability assessments using different protective agents.

REFERENCES

- (1) Massari, S.; Ruberti, M. Rare Earth Elements as Critical Raw Materials: Focus on International Markets and Future Strategies. *Resour. Policy* **2013**, *38* (1), 36–43.
- (2) Graedel, T. E.; Harper, E. M.; Nassar, N. T.; Reck, B. K. On the Materials Basis of Modern Society. *Proc. Natl. Acad. Sci. U. S. A.* **2015**, *112* (20), 6295–6300.
- (3) Hosono, H.; Hayashi, K.; Kamiya, T.; Atou, T.; Susaki, T. New Functionalities in Abundant Element Oxides: Ubiquitous Element Strategy. *Science and Technology of Advanced Materials* **2011**, *12* (3), 034303.
- (4) Nassar, N. T.; Graedel, T. E.; Harper, E. M. By-Product Metals Are Technologically Essential but Have Problematic Supply. *Sci. Adv.* **2015**, *1* (3), e1400180.
- (5) Yeh, J.-W. Alloy Design Strategies and Future Trends in High-Entropy Alloys. *JOM* **2013**, *65* (12), 1759–1771.
- (6) Ding, Q.; Zhang, Y.; Chen, X.; Fu, X.; Chen, D.; Chen, S.; Gu, L.; Wei, F.; Bei, H.; Gao, Y.; Wen, M.; Li, J.; Zhang, Z.; Zhu, T.; Ritchie, R. O.; Yu, Q. Tuning Element Distribution, Structure and Properties by Composition in High-Entropy Alloys. *Nature* **2019**, *574* (7777), 223–227.
- (7) Sohrabi, M. J.; Kalhor, A.; Mirzadeh, H.; Rodak, K.; Kim, H. S. Tailoring the Strengthening Mechanisms of High-Entropy Alloys toward Excellent Strength-Ductility Synergy by Metalloid Silicon Alloying: A Review. *Prog. Mater. Sci.* **2024**, *144* (101295), 101295.

- (8) Liu, C.; Lu, W.; Xia, W.; Du, C.; Rao, Z.; Best, J. P.; Brinckmann, S.; Lu, J.; Gault, B.; Dehm, G.; Wu, G.; Li, Z.; Raabe, D. Massive Interstitial Solid Solution Alloys Achieve Near-Theoretical Strength. *Nat. Commun.* **2022**, *13* (1), 1102.
- (9) Han, Y.; Kong, F. L.; Han, F. F.; Inoue, A.; Zhu, S. L.; Shalaan, E.; Al-Marzouki, F. New Fe-Based Soft Magnetic Amorphous Alloys with High Saturation Magnetization and Good Corrosion Resistance for Dust Core Application. *Intermetallics* **2016**, *76*, 18–25.
- (10) Rao, Z.; Dutta, B.; Körmann, F.; Lu, W.; Zhou, X.; Liu, C.; Silva, A. K.; Wiedwald, U.; Spasova, M.; Farle, M.; Ponge, D.; Gault, B.; Neugebauer, J.; Raabe, D.; Li, Z. Beyond Solid Solution High - entropy Alloys: Tailoring Magnetic Properties via Spinodal Decomposition. *Adv. Funct. Mater.* **2021**, *31* (7), 2007668.
- (11) Jin, K.; Sales, B. C.; Stocks, G. M.; Samolyuk, G. D.; Daene, M.; Weber, W. J.; Zhang, Y.; Bei, H. Tailoring the Physical Properties of Ni-Based Single-Phase Equiatomic Alloys by Modifying the Chemical Complexity. *Sci. Rep.* **2016**, *6* (1), 20159.
- (12) Kusada, K.; Kobayashi, H.; Ikeda, R.; Kubota, Y.; Takata, M.; Toh, S.; Yamamoto, T.; Matsumura, S.; Sumi, N.; Sato, K.; Nagaoka, K.; Kitagawa, H. Solid Solution Alloy Nanoparticles of Immiscible Pd and Ru Elements Neighboring on Rh: Changeover of the Thermodynamic Behavior for Hydrogen Storage and Enhanced CO-Oxidizing Ability. *J. Am. Chem. Soc.* **2014**, *136* (5), 1864–1871.
- (13) Sato, K.; Tomonaga, H.; Yamamoto, T.; Matsumura, S.; Zulkifli, N. D. B.; Ishimoto, T.; Koyama, M.; Kusada, K.; Kobayashi, H.; Kitagawa, H.; Nagaoka, K. A Synthetic Pseudo-Rh: NO_x Reduction Activity and Electronic Structure of Pd–Ru Solid-Solution Alloy Nanoparticles. *Sci. Rep.* **2016**, *6*, 28265.

- (14) Yao, Y.; Huang, Z.; Xie, P.; Lacey, S. D.; Jacob, R. J.; Xie, H.; Chen, F.; Nie, A.; Pu, T.; Rehwoldt, M.; Yu, D.; Zachariah, M. R.; Wang, C.; Shahbazian-Yassar, R.; Li, J.; Hu, L. Carbothermal Shock Synthesis of High-Entropy-Alloy Nanoparticles. *Science* **2018**, *359* (6383), 1489–1494.
- (15) Zhao, M.; Lyu, Z.; Xie, M.; Hood, Z. D.; Cao, Z.; Chi, M.; Xia, Y. Pd - Ru Alloy Nanocages with a Face - centered Cubic Structure and Their Enhanced Activity toward the Oxidation of Ethylene Glycol and Glycerol. *Small Methods* **2020**, *4* (5), 1900843.
- (16) Song, C.; Tayal, A.; Seo, O.; Kim, J.; Chen, Y.; Hiroi, S.; Kumara, L. S. R.; Kusada, K.; Kobayashi, H.; Kitagawa, H.; Sakata, O. Correlation between the Electronic/Local Structure and CO-Oxidation Activity of Pd x Ru_{1-x} Alloy Nanoparticles. *Nanoscale Adv* **2019**, *1* (2), 546–553.
- (17) Minamihara, H.; Kusada, K.; Yamamoto, T.; Toriyama, T.; Murakami, Y.; Matsumura, S.; Kumara, L. S. R.; Sakata, O.; Kawaguchi, S.; Kubota, Y.; Seo, O.; Yasuno, S.; Kitagawa, H. Continuous-Flow Chemical Synthesis for Sub-2 Nm Ultra-Multielement Alloy Nanoparticles Consisting of Group IV to XV Elements. *J. Am. Chem. Soc.* **2023**, *145* (31), 17136–17142.
- (18) Zhu, X.; Guo, Q.; Sun, Y.; Chen, S.; Wang, J.-Q.; Wu, M.; Fu, W.; Tang, Y.; Duan, X.; Chen, D.; Wan, Y. Optimising Surface d Charge of AuPd Nanoalloy Catalysts for Enhanced Catalytic Activity. *Nat. Commun.* **2019**, *10* (1), 1428.
- (19) Jørgensen, M.; Grönbeck, H. Selective Acetylene Hydrogenation over Single-Atom Alloy Nanoparticles by Kinetic Monte Carlo. *J. Am. Chem. Soc.* **2019**, *141* (21), 8541–8549.
- (20) Wang, L.; Hasanzadeh Kafshgari, M.; Meunier, M. Optical Properties and Applications of Plasmonic - metal Nanoparticles. *Adv. Funct. Mater.* **2020**, *30* (51), 2005400.

- 589 (21) Han, M.; Maleski, K.; Shuck, C. E.; Yang, Y.; Glazar, J. T.; Foucher, A. C.;
590 Hantanasirisakul, K.; Sarycheva, A.; Frey, N. C.; May, S. J.; Shenoy, V. B.; Stach, E. A.;
591 Gogotsi, Y. Tailoring Electronic and Optical Properties of MXenes through Forming Solid
592 Solutions. *J. Am. Chem. Soc.* **2020**, *142* (45), 19110–19118.
- 593 (22) Nugroho, F. A. A.; Darmadi, I.; Zhdanov, V. P.; Langhammer, C. Universal Scaling and
594 Design Rules of Hydrogen-Induced Optical Properties in Pd and Pd-Alloy Nanoparticles. *ACS*
595 *Nano* **2018**, *12* (10), 9903–9912.
- 596 (23) Yadav, T. P.; Yadav, R. M.; Singh, D. P. Mechanical Milling: A Top Down Approach for
597 the Synthesis of Nanomaterials and Nanocomposites. *Nanosci. Nanotechnol. Lett.* **2012**, *2* (3),
598 22–48.
- 599 (24) Wang, B.; Wang, C.; Yu, X.; Cao, Y.; Gao, L.; Wu, C.; Yao, Y.; Lin, Z.; Zou, Z. General
600 Synthesis of High-Entropy Alloy and Ceramic Nanoparticles in Nanoseconds. *Nature Synthesis*
601 **2022**, *1* (2), 138–146.
- 602 (25) Grammatikopoulos, P.; Steinhauer, S.; Vernieres, J.; Singh, V.; Sowwan, M.
603 Nanoparticle Design by Gas-Phase Synthesis. *Adv. Phys. X.* **2016**, *1* (1), 81–100.
- 604 (26) Mantzaris, N. V. Liquid-Phase Synthesis of Nanoparticles: Particle Size Distribution
605 Dynamics and Control. *Chem. Eng. Sci.* **2005**, *60* (17), 4749–4770.
- 606 (27) Kusada, K.; Yamauchi, M.; Kobayashi, H.; Kitagawa, H.; Kubota, Y. Hydrogen-Storage
607 Properties of Solid-Solution Alloys of Immiscible Neighboring Elements with Pd. *J. Am. Chem.*
608 *Soc.* **2010**, *132* (45), 15896–15898.

- 609 (28) Kusada, K.; Yamamoto, T.; Toriyama, T.; Matsumura, S.; Sato, K.; Nagaoka, K.; Terada,
610 K.; Ikeda, Y.; Hirai, Y.; Kitagawa, H. Nonequilibrium Flow-Synthesis of Solid-Solution Alloy
611 Nanoparticles: From Immiscible Binary to High-Entropy Alloys. *J. Phys. Chem. C* **2021**, *125* (1),
612 458–463.
- 613 (29) Mashimo, T.; Tamura, S.; Yamamoto, K.; Kelgenbaeva, Z.; Ma, W.; Tokuda, M.;
614 Koinuma, M.; Isobe, H.; Yoshiasa, A. Synthesis of Pd-Ru Solid-Solution Nanoparticles by
615 Pulsed Plasma in Liquid Method. *RSC Adv.* **2020**, *10* (22), 13232–13236.
- 616 (30) Fukushima, T.; Tsukuda, R.; Ohhashi, S.; Fujita, N.; Kameoka, S. One-Step Synthesis of
617 Non-Equilibrium Pd-Ru Alloys from Al-Pd-Ru Quasicrystals and Approximants. *J. Phys. Conf.*
618 *Ser.* **2023**, *2461* (1), 012001.
- 619 (31) Essinger-Hileman, E. R.; DeCicco, D.; Bondi, J. F.; Schaak, R. E. Aqueous Room-
620 Temperature Synthesis of Au–Rh, Au–Pt, Pt–Rh, and Pd–Rh Alloy Nanoparticles: Fully Tunable
621 Compositions within the Miscibility Gaps. *J. Mater. Chem.* **2011**, *21* (31), 11599.
- 622 (32) Sun, L.; Cao, D.; Wang, G. Pd–Ru/C as the Electrocatalyst for Hydrogen Peroxide
623 Reduction. *J. Appl. Electrochem.* **2008**, *38* (10), 1415–1419.
- 624 (33) Shimada, I.; Oshima, Y.; Otomo, J. Reaction Analysis of Ethanol Electro-Oxidation on
625 PdRu/C Catalyst at Intermediate Temperature. *J. Chem. Eng. Jpn.* **2014**, *47* (7), 514–520.
- 626 (34) Monyoncho, E. A.; Ntais, S.; Soares, F.; Woo, T. K.; Baranova, E. A. Synergetic Effect
627 of Palladium–Ruthenium Nanostructures for Ethanol Electrooxidation in Alkaline Media. *J.*
628 *Power Sources* **2015**, *287*, 139–149.

629 (35) Chen, P.-C.; Gao, M.; McCandler, C. A.; Song, C.; Jin, J.; Yang, Y.; Maulana, A. L.;
630 Persson, K. A.; Yang, P. Complete Miscibility of Immiscible Elements at the Nanometre Scale.
631 *Nat. Nanotechnol.* **2024**, *19* (6), 775–781.

632 (36) Nanba, Y.; Koyama, M. Thermodynamic Stability of Pd-Ru Alloy Nanoparticles:
633 Combination of Density Functional Theory Calculations, Supervised Learning, and Wang-
634 Landau Sampling. *Phys. Chem. Chem. Phys.* **2022**, *24* (25), 15452–15461.

635 (37) Nagasawa, H.; Aoki, N.; Mae, K. Design of a New Micromixer for Instant Mixing Based
636 on the Collision of Micro Segments. *Chem. Eng. Technol.* **2005**, *28* (3), 324–330.

637 (38) Watanabe, S.; Ohsaki, S.; Fukuta, A.; Hanafusa, T.; Takada, K.; Tanaka, H.; Maki, T.;
638 Mae, K.; Miyahara, M. T. Characterization of Mixing Performance in a Microreactor and Its
639 Application to the Synthesis of Porous Coordination Polymer Particles. *Adv. Powder Technol.*
640 **2017**, *28* (11), 3104–3110.

641 (39) Asano, S.; Maki, T.; Inoue, S.; Sogo, S.; Furuta, M.; Watanabe, S.; Muranaka, Y.; Kudo,
642 S.; Hayashi, J.-I.; Mae, K. Incorporative Mixing in Microreactors: Influence on Reactions and
643 Importance of Inlet Designation. *Chem. Eng. J.* **2023**, *451* (138942), 138942.

644 (40) Watanabe, S.; Koshiyama, T.; Watanabe, T.; Miyahara, M. T. Room-Temperature
645 Synthesis of Ni and Pt-Co Alloy Nanoparticles Using a Microreactor. *Front. Chem. Eng.* **2021**, *3*,
646 780384.

647 (41) Maw, S. S.; Watanabe, S.; Miyahara, M. T. Flow Synthesis of Silver Nanoshells Using a
648 Microreactor. *Chem. Eng. J.* **2019**, *374*, 674–683.

- 649 (42) Watanabe, S.; Hiratsuka, T.; Asahi, Y.; Tanaka, A.; Mae, K.; Miyahara, M. T. Flow
650 Synthesis of Plasmonic Gold Nanoshells via a Microreactor. *Part. Part. Syst. Charact.* **2015**, 32
651 (2), 234–242.
- 652 (43) Watanabe, S.; Hiraide, S.; Arima, H.; Fukuta, A.; Mori, M.; Tanaka, H.; Miyahara, M. T.
653 Size-Dependent Guest-Memory Switching of the Flexible and Robust Adsorption Characteristics
654 of Layered Metal-Organic Frameworks. *Sci. Adv.* **2024**, 10 (49), eadr1387.
- 655 (44) Watanabe, S.; Ohsaki, S.; Hanafusa, T.; Takada, K.; Tanaka, H.; Mae, K.; Miyahara, M.
656 T. Synthesis of Zeolitic Imidazolate Framework-8 Particles of Controlled Sizes, Shapes, and
657 Gate Adsorption Characteristics Using a Central Collision-Type Microreactor. *Chem. Eng. J.*
658 **2017**, 313, 724–733.
- 659 (45) Fournier, M.-C.; Falk, L.; Villiermaux, J. A New Parallel Competing Reaction System for
660 Assessing Micromixing Efficiency—Determination of Micromixing Time by a Simple Mixing
661 Model. *Chem. Eng. Sci.* **1996**, 51 (23), 5187–5192.
- 662 (46) Commenge, J.-M.; Falk, L. Villiermaux–Dushman Protocol for Experimental
663 Characterization of Micromixers. *Chemical Engineering and Processing: Process Intensification*
664 **2011**, 50 (10), 979–990.
- 665 (47) Schneider, C. A.; Rasband, W. S.; Eliceiri, K. W. NIH Image to ImageJ: 25 Years of
666 Image Analysis. *Nat. Methods* **2012**, 9 (7), 671–675.
- 667 (48) Kawaguchi, S.; Takemoto, M.; Osaka, K.; Nishibori, E.; Moriyoshi, C.; Kubota, Y.;
668 Kuroiwa, Y.; Sugimoto, K. High-Throughput Powder Diffraction Measurement System

669 Consisting of Multiple MYTHEN Detectors at Beamline BL02B2 of SPring-8. *Rev. Sci. Instrum.*
670 **2017**, 88 (8), 085111.

671 (49) Kawaguchi, S.; Kobayashi, S.; Yamada, H.; Ashitani, H.; Takemoto, M.; Imai, Y.; Hatsui,
672 T.; Sugimoto, K.; Sakata, O. High-Throughput and High-Resolution Powder X-Ray
673 Diffractometer Consisting of Six Sets of 2D CdTe Detectors with Variable Sample-to-Detector
674 Distance and Innovative Automation System. *J. Synchrotron Radiat.* **2024**, 31 (Pt 4), 955–967.

675 (50) Izumi, F.; Momma, K. Three-Dimensional Visualization in Powder Diffraction. *Solid*
676 *State Phenom.* **2007**, 130, 15–20.

677 (51) Toraya, B. Y. H. Whole-Powder-Pattern Fitting without Reference to a Structural Model:
678 Application to X-Ray Powder Diffraction Data. *J. Appl. Crystallogr.* **1986**, 19, 440–447.

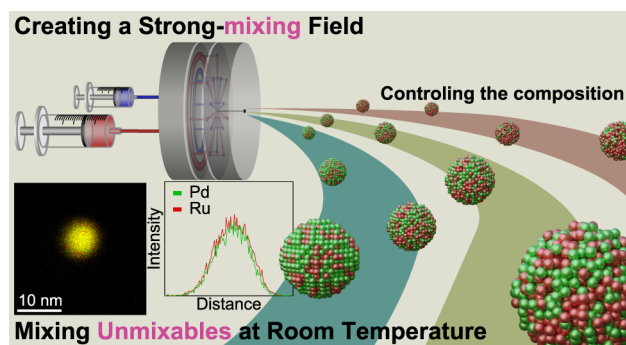
679 (52) Halder, N. C.; Wagner, C. N. J. Separation of Particle Size and Lattice Strain in Integral
680 Breadth Measurements. *Acta Crystallogr.* **1966**, 20 (2), 312–313.

681 (53) Halder, N. C.; Wagner, C. N. J. Analysis of the Broadening of Powder Pattern Peaks
682 Using Variance, Integral Breadth, and Fourier Coefficients of the Line Profile. In *Advances in X-*
683 *Ray Analysis*; Springer US: Boston, MA, 1966; pp 91–102.

684 (54) Sun, J.; Leff, A.; Li, Y.; Woehl, T. J. Visualizing Formation of High Entropy Alloy
685 Nanoparticles with Liquid Phase Transmission Electron Microscopy. *Nanoscale* **2023**, 15 (24),
686 10447–10457.

687 (55) Zhang, Q.; Kusada, K.; Wu, D.; Yamamoto, T.; Toriyama, T.; Matsumura, S.;
688 Kawaguchi, S.; Kubota, Y.; Kitagawa, H. Selective Control of Fcc and Hcp Crystal Structures in
689 Au-Ru Solid-Solution Alloy Nanoparticles. *Nat. Commun.* **2018**, 9 (1), 510.

690 **TABLE OF CONTENTS GRAPHIC**



691