

Rapid and Continuous Polyol Process for Platinum Nanoparticle Synthesis Using a Single-mode Microwave Flow Reactor

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Rapid and continuous synthesis of size-controlled platinum nanoparticles is achieved using a single-mode microwave flow reactor controlled with temperature feedback module. Platinum nanoparticles are synthesized within 2.8 s of residence time in glycerol and 1,3-propanediol having large dielectric dissipation factor and high solvent viscosity.

Platinum nanoparticles have numerous industrial applications, particularly as catalysts for use in chemical industry,¹ automobile emission gas control,² and as electrocatalysts for low-temperature fuel cells.³ An efficient process suitable for the large-scale production of platinum nanoparticles with uniform size distribution is in strong demand from a practical perspective. To achieve facile reduction, stronger reducing agents such as NaBH₄ and hydrazine have often been used for platinum nanoparticle synthesis.⁴ Unlike such toxic chemicals, polyols including glycerol and 1,3-propanediol are safe reducing agents. However, because of their mild reducing ability, high temperatures and long reaction times are necessary to reduce platinum precursors.⁵

Enhancement of the reaction rate using microwave (MW) heating has been anticipated recently; it is becoming an established procedure in inorganic and organic syntheses.^{6,7} Reaction rates are increased by 1–2 orders of magnitude compared to conventional heating.⁸ For example, synthesis of platinum nanoparticles using polyol processing has been accelerated by MW heating to enable completion within a few minutes.^{8–12} Despite remarkable MW-induced effects, most equipment used to date is for batch-type processing. In contrast, continuous processing by using flow-type MW reactors is more suitable for scale up production. Nevertheless, most flow reactors originate from batch systems with multimode cavities in which the MW density is not homogeneous.¹³ Consequently, uniform heating throughout the reactor cannot be guaranteed particularly under long-term operation. The authors have developed a MW system that can form a uniform electric field in a cylindrical single-mode MW cavity.¹⁴ Using this system, we have demonstrated the continuous synthesis of silver nanoparticles based on a polyol process.¹⁵ It is important to provide a methodology that is adaptable to large-scale production of platinum nanoparticles. Consequently, we attempted the rapid and continuous flow synthesis of platinum nanoparticles of constant quality using our single-mode MW cavity reactor.

Our original MW reactor system is composed of a variable-frequency generator, field intensity monitor, temperature sensor, and a cylindrical single-mode aluminum cavity (see Supporting Information¹⁶). The oscillation frequency was automatically

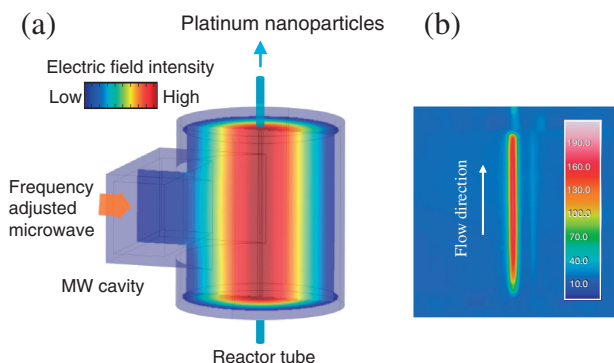


Figure 1. a) Electric field distribution in the MW cavity calculated by computational simulation on the COMSOL Multiphysics program. b) Thermographic observation of the reactor tube during the flow reaction in ethylene glycol solution (160 °C). Flow rate: 10 mL h⁻¹, Ethylene glycol solution contains H₂[PtCl₆]·6H₂O (10 mM) and 1 wt % PVP.

adjusted for matching with the resonance frequency by analyzing with the field monitor, and the applied power was controlled by the temperature feedback module. As the result, a uniform and intense electric field (heating zone) was formed along the reactor tube located in the central line of the cylindrical cavity (Figure 1a).

Platinum nanoparticles were synthesized by introduction of a polyol solution containing H₂[PtCl₆]·6H₂O and poly(*N*-vinylpyrrolidone) (PVP) into the reactor tube. We used ethylene glycol, glycerol, and 1,3-propanediol which works as a reducing agent and as a reaction solvent. The solution temperature increased instantaneously, reaching the setting point with high precision (±1 °C) in a few seconds. Thermographic measurement in Figure 1b depicts the homogeneous temperature distribution in the reactor tube indicating the uniform heating of ethylene glycol solution.

Figure 2a shows UV–vis spectra of the platinum nanoparticle dispersions prepared in ethylene glycol by varying the flow rate 3–50 mL h⁻¹ while maintaining the temperature at 160 °C. A typical peak at around 260 nm is associated with the absorption of the PtCl₆²⁻ ion.^{10,11,17} Peak intensity decreased associated with the reduction of PtCl₆²⁻. Therefore, we followed this absorption peak for the monitor of platinum nanoparticle formation. The absorption peak disappeared completely at a flow rate of less than 10 mL h⁻¹ (residence time 28.3 s), indicating that PtCl₆²⁻ ion was reduced entirely to Pt⁰.^{10,11,17} A typical TEM image in Figure 2b portrays the formation of monodispersed nanoparticles. Nanoparticles of 5.9-nm average sizes

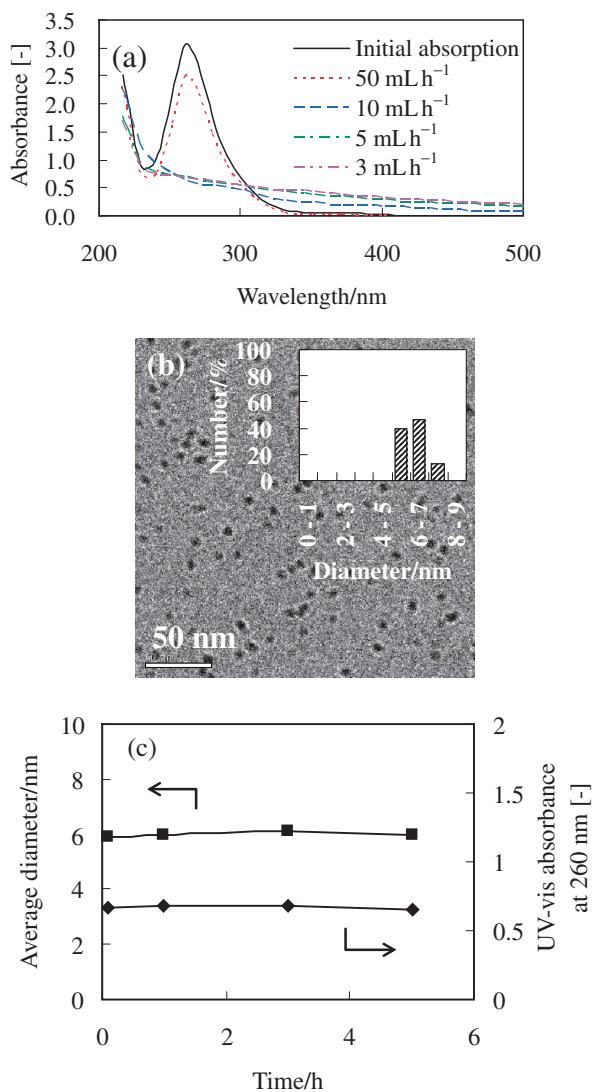


Figure 2. a) UV-vis spectra of platinum nanoparticle dispersions prepared at various flow rate. $\text{H}_2[\text{PtCl}_6] \cdot 6\text{H}_2\text{O}$ (10 mM) and PVP (1 wt %) in ethylene glycol. b) TEM image of the platinum nanoparticles synthesized at a flow rate of 10 mL h^{-1} (160°C). c) Time dependence of average diameter of platinum nanoparticles and UV-vis absorbance of the dispersed solution. Flow rate: 10 mL h^{-1} .

were obtained with the relative standard deviation of 0.12 as shown in the particle size histogram (inset). Figure 2c shows the time profile of the absorbance at 260 nm and the average particle diameter. The reaction was continued for 5 h without significant change of particle size with a constant reaction yield that is closely correlated with the absorbance. Such a steady reaction was attained by control of nucleation and subsequent crystal growth under homogeneous MW irradiation to the reaction solution.

Figure 3a portrays UV-vis spectra of platinum nanoparticle dispersion prepared in glycerol with the flow rate of $10\text{--}100 \text{ mL h}^{-1}$. The absorption peak at around 260 nm disappeared even with 100 mL h^{-1} (residence time 2.8 s in the MW heating zone) at 160°C . This indicates that the reaction rate in glycerol was

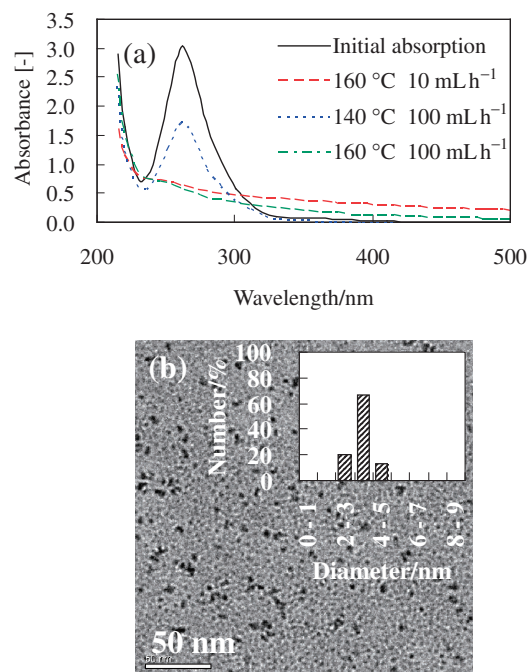


Figure 3. a) UV-vis spectra of platinum nanoparticle dispersions with the $10\text{--}100 \text{ mL h}^{-1}$ flow rate prepared in the glycerol solution of $\text{H}_2[\text{PtCl}_6] \cdot 6\text{H}_2\text{O}$ (10 mM) including PVP (1 wt %). b) Typical TEM image of platinum nanoparticles synthesized at a flow rate of 100 mL h^{-1} (160°C).

about 10 times higher than that observed in ethylene glycol at the same reaction temperature. Under the increased flow rate, platinum nanoparticles of 3.4 nm with the relative standard deviation of 0.17 were obtained as presented in Figure 3b. The magnitude of heating has been thought to depend on the dielectric dissipation factor (loss tangent value) of the molecule. The loss tangent values of ethylene glycol and glycerol are 1.35 and 0.65, respectively at 25°C under 2.45 GHz of MW frequency.⁶ According to the dielectric loss property, ethylene glycol can be heated much more rapidly than glycerol. The superior rate enhancement of platinum nanoparticle formation observed in glycerol over that in ethylene glycol is inconsistent with the order of the loss tangent value.¹⁸ We interpreted this anomaly in connection with the remarkably high viscosity of glycerol (934 mPa s) compared to that of ethylene glycol (16 mPa s).¹⁹ The solvent viscosity is reflected by intermolecular hydrogen-bond networks that restrict the free molecular motions.⁶ Metal nuclei initially generated preferentially absorb MW energy and form localized high temperature in a microscopic area.²⁰ Such hot spots associated with preferential heating can be maintained stably in a highly viscous medium by slow thermal diffusion, thereby localized thermal energy can induce direct heating of nucleation sites and facilitate particle formation reaction.

Figure 4 shows UV-vis spectra of the platinum dispersion prepared in 1,3-propanediol solution. The peak almost disappeared at 160°C with a flow rate of 200 mL h^{-1} which corresponds to the residence time of 1.4 s in the MW heating zone. The remarkably rapid reaction observed in 1,3-propanediol is consistent with the hypothesis presented above, i.e., slow

Table 1. Various polyol synthesis of platinum nanoparticles protected by PVP

Entry	Polyols ^a	Heating type	Temp /°C	Time /s ^c	H ₂ [PtCl ₆] [·] 6H ₂ O /mM	Particle size /nm	Relative standard deviation	Reference
1	EG	Oil bath, batch	176	720	ca. 1.0	1.1–2.7	0.27–0.28	9
2	EG	M.W., batch	176	30	ca. 1.0	1.9–3.8	0.15–0.19	9
3	EG	M.W., batch	150	900	ca. 0.9	4–5	—	8
4	EG	M.W., flow ^b	—	15	ca. 0.8	1.46	0.17	11
5	GCL	M.W., batch	290	120	ca. 110	2.0	—	12
6	EG	M.W., flow	160	28.3	10	5.9	0.12	This work
7	GCL	M.W., flow	160	28.3	10	6.5	0.18	This work
8	GCL	M.W., flow	160	2.8	10	3.4	0.17	This work
9	1,3-PD	M.W., flow	160	2.8	10	4.1	0.10	This work

^aEG, GCL, and 1,3-PD denote ethylene glycol, glycerol, and 1,3-propanediol, respectively. ^bTubular reactor was installed in a conventional MW oven. ^cResidence time for the flow reaction.

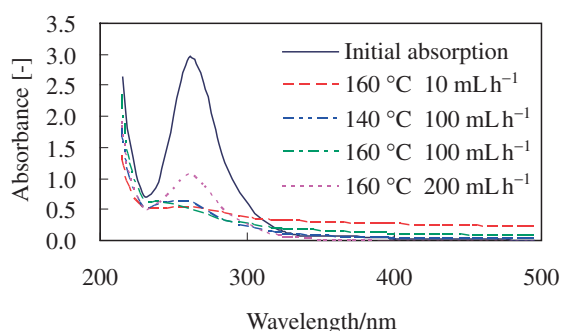


Figure 4. UV-vis spectra of platinum nanoparticle dispersions prepared at various flow rates. H₂[PtCl₆][·]6H₂O (10 mM) and PVP (1 wt %) in 1,3-propanediol.

thermal diffusion of directly heated nucleation sites generates hot spots which induce rapid particle growth. In addition to the large loss tangent value of 1,3-propanediol (1.30), which is comparable to that of ethylene glycol (1.35), its viscosity is also large (56 mPa).^{6,19} Therefore, the notable rate enhancement can be attributed to the combined effect of large loss tangent value and slow thermal diffusion in highly viscous 1,3-propanediol.

Table 1 presents the performance of platinum nanoparticle synthesis used in this study along with those reported in the precedent work.^{8,9,11,12} In spite of rapid flow rate and high concentration of platinum feed, our reactor system steadily yielded size-controlled platinum nanoparticles. Particularly, 4.1-nm particles with the relative standard deviation of 0.10 are produced continuously in 1,3-propanediol with residence time of 2.8 s. The particle size decreased concomitantly with the increase of the flow rate, presumably because the limited reaction time restricts the particle growth after initial nucleation.

In conclusion, the present MW-assisted flow reactor system combined with the appropriate polyol provides an elegant methodology for continuous and steady production of platinum nanoparticles with constant quality.

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