

Electronic Supplementary Information for

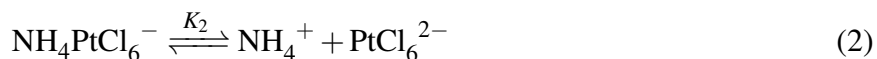
Precursor-templated synthesis of thermodynamically unfavored platinum nanoplates for the oxygen reduction reaction

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Ammonium hexachloroplatinate ((NH₄)₂PtCl₆) exhibits a unique characteristic in aqueous solutions. It dissolves well in water, while easily precipitates from a NH₄Cl solution. The dissolution mechanism should be described by the following equations:



K_1 and K_2 in the equations denote equilibrium constants. According to Eq. 1 and Eq. 2, a saturated Pt ion concentration (c_p) in an aqueous solution can be predicted as

$$c_p = \frac{K_1}{c_a} + \frac{K_1 K_2}{c_a^2} \quad (3)$$

where c_a represents the NH₄⁺ ion concentration. However, its behavior is not quantitatively understood. Prior to exploring the precursor-templated synthesis of Pt nanoplates, we investigated the dissolution/precipitation behavior of (NH₄)₂PtCl₆.

Aqueous NH₄Cl solutions with different concentrations were prepared, and a saturated amount of (NH₄)₂PtCl₆ was added to each solution. The solutions were kept at 30 °C for a few days, followed by filtration. Afterwards, the Pt ion concentration was measured by ICP-AES to derive the soluble amount.

Fig. S1 (a) shows the solubility of (NH₄)₂PtCl₆ as a function of the NH₄Cl concentration. The plots were fitted by Eq. 3. It should be noted that the fitting parameters directly provide the equilibrium constants, enabling a quantitative discussion on the dissolution/precipitation behavior of (NH₄)₂PtCl₆. Table S1 summarizes the values of K_1 and K_2 along with those at different temperatures.

Then we calculated the dissolution/precipitation ratio of the Pt species in arbitrary aqueous solutions. Fig. S1 (b) shows the proportion of ionic Pt to the total Pt. The calculation suggests that more than 95 % of Pt exists as a precipitated salt under the synthesis condition of Pt nanoplates (total Pt: 1.2 mmol L⁻¹, NH₄Cl: 3000 mmol L⁻¹).

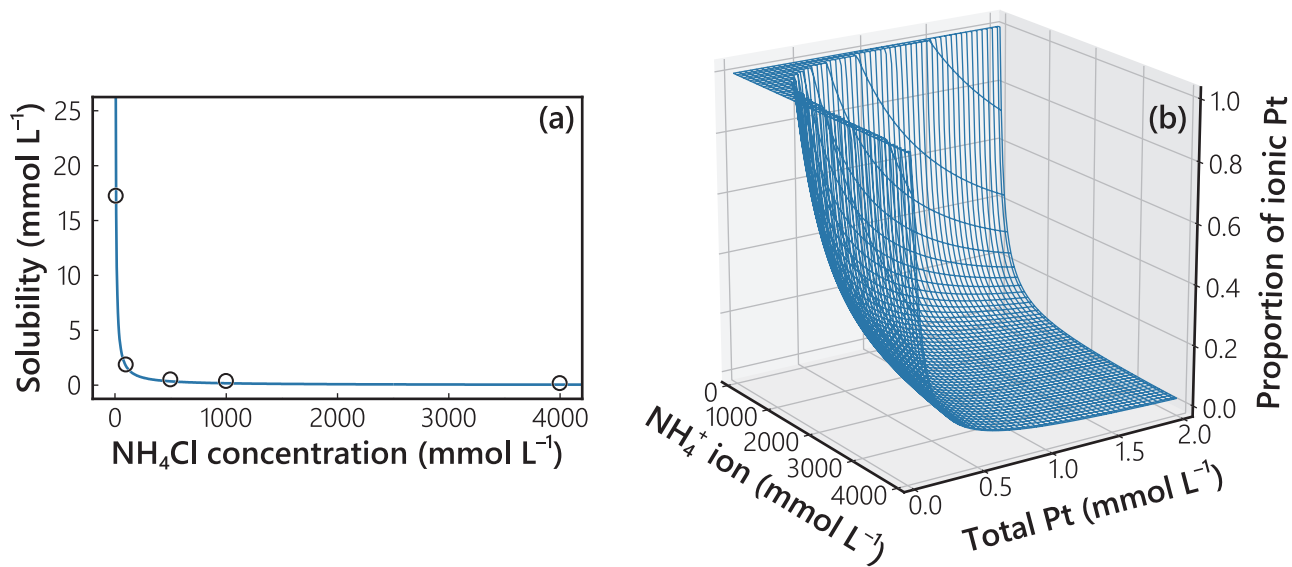


Fig. S1 (a) Solubility of $(\text{NH}_4)_2\text{PtCl}_6$ as a function of the NH_4Cl concentration. (b) Proportion of ionic Pt to the total Pt calculated for an aqueous solution containing arbitrary concentrations of the NH_4^+ ion and Pt source.

Table S1 Equilibrium constants for the dissolution reaction of $(\text{NH}_4)_2\text{PtCl}_6$ in water at different temperatures

Temperature ($^{\circ}\text{C}$)	K_1 (mmol L^{-1})	K_2 (mmol L^{-1})
10	81.164	4.181
30	172.395	0.000
50	283.289	0.000
70	350.067	0.000

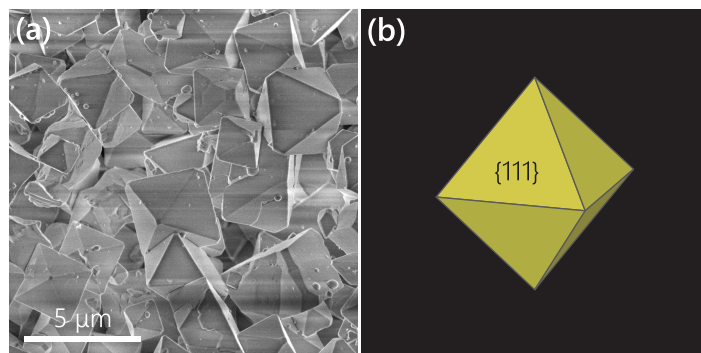


Fig. S2 (a) SEM image and (b) illustration of $(\text{NH}_4)_2\text{PtCl}_6$. Octahedral shape enclosed by eight $\{111\}$ facets is observed.

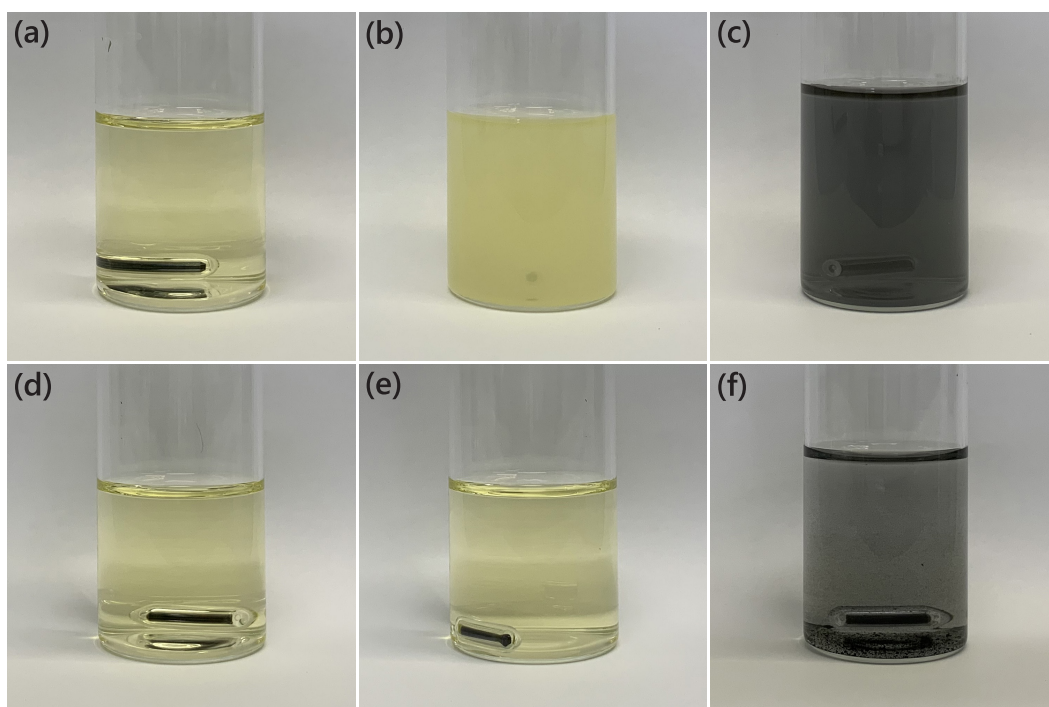


Fig. S3 Synthesis process of (a)–(c) Pt nanoplates from the precipitated Pt precursor, and (d)–(f) Pt nanoparticles from the dissolved Pt precursor. Synthesis solutions (a)(d) just after preparation, (b)(e) thoroughly stirred, and (c)(f) completed reaction.

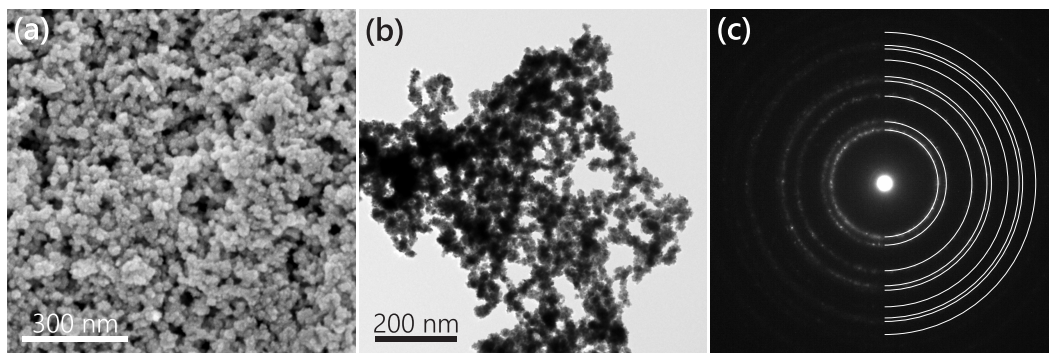


Fig. S4 (a) SEM and (b) TEM images, and (c) SAED pattern of Pt nanoparticles synthesized from the dissolved Pt precursor. H_2PtCl_6 was reduced by NaBH_4 in water without NH_4Cl . Model diffraction rings represent the fcc Pt $\{111\}$, $\{200\}$, $\{220\}$, $\{311\}$, $\{222\}$, $\{400\}$, $\{331\}$, $\{420\}$, and $\{422\}$ planes in order from the center.

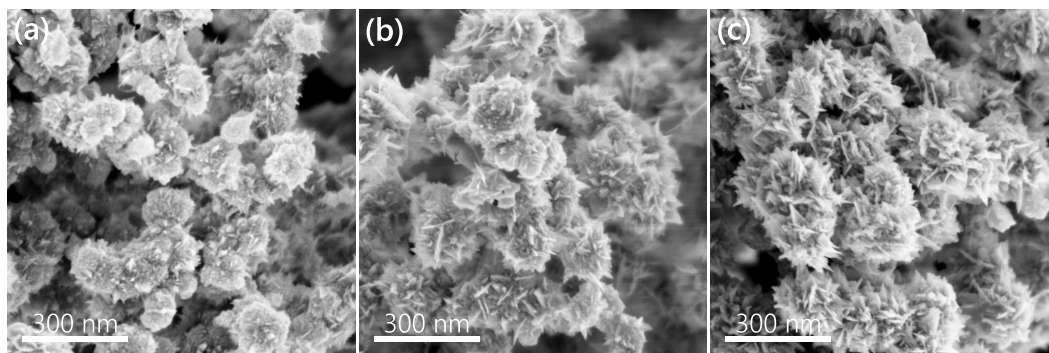


Fig. S5 SEM images of Pt nanoparticles synthesized from a mixture of precipitated and dissolved Pt precursors. Proportion of the precipitated precursor is controlled at (a) 25, (b) 50, and (c) 75 % by adjusting the NH_4Cl concentration to 192, 287, and 575 mmol L^{-1} , respectively.

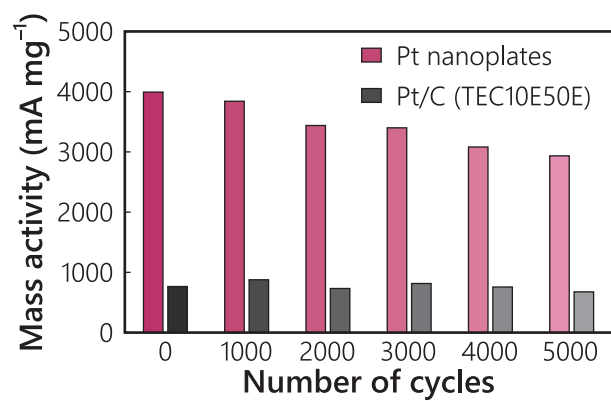


Fig. S6 Change in mass activity of Pt nanoplates and the commercial Pt/C at 0.85 V vs. RHE during the potential cycles.

Table S2 Electrochemical properties of Pt nanoplates and the commercial Pt/C towards the ORR before and after 5000 potential cycles

Sample name	ECSA ($\text{m}^2 \text{g}^{-1}$)	Mass activity (mA mg^{-1}) at 0.90, 0.85 $V_{\text{vs.RHE}}$	Specific activity (mA cm^{-2}) at 0.90, 0.85 $V_{\text{vs.RHE}}$
Pt nanoplates (before)	25.7	449, 4010	1.75, 15.63
Pt nanoplates (after)	16.0	368, 2947	2.31, 18.46
Pt/C (before)	57.2	299, 768	0.52, 1.34
Pt/C (after)	33.9	200, 679	0.59, 2.00

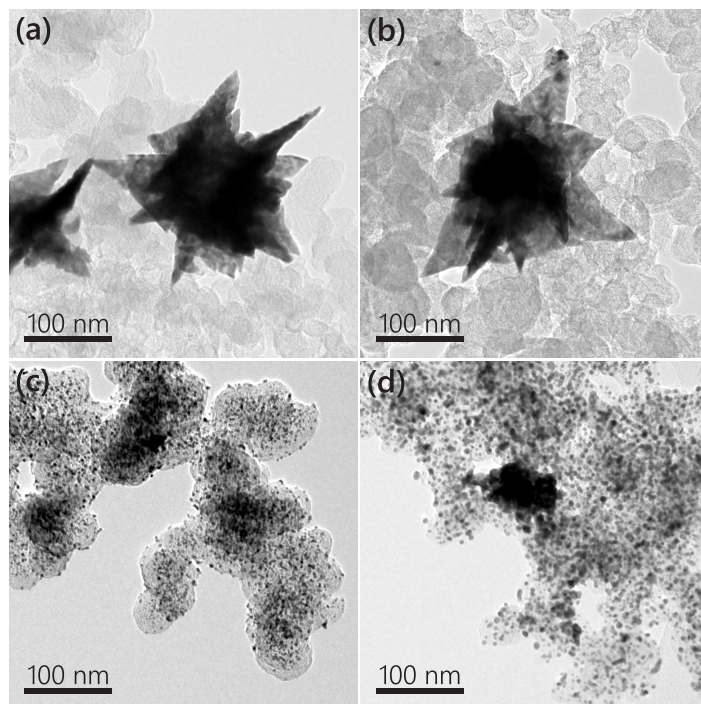


Fig. S7 TEM images of (a)(b) carbon-deposited Pt nanoplates and (c)(d) the commercial Pt/C (a)(c) before and (b)(d) after the stability test.