

**Electronic Supplementary Information (ESI)
for**

**Synthesis of Shaped Pt Nanoparticles Using Common Anions or Small
Molecules as Shape-Directing Agents: Observation of a Strong Halide or
Pseudo-halide Effect**

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A. Pt colloid synthesis procedures

Non-aqueous glycolate-protected nanoparticles using Zeise's dimer

To prepare tetrabutylammonium glycolate, 1.465 g glycolic acid was added directly to 12.63 mL of a 40% w/w aqueous solution of tetrabutylammonium hydroxide. The resulting salt was extracted with 40mL methylene chloride 8 times, dried over magnesium sulfate, and isolated by removal of the solvent under vacuum. In a typical preparation of non-aqueous glycolate-protected nanoparticles, 7.35 mg (1.25×10^{-6} mol) di- μ -chloro-dichlorobis(ethylene)diplatinum(II) (Zeise's dimer) was dissolved in 25 mL THF along with 8.0 mg tetrabutylammonium glycolate (4 eq.) The solution was then heated at 60 °C for approximately 5 min until the golden color of nanoparticulate platinum indicated completion of the reaction. See Figure S1.

Aqueous glycolate and tartrate protected nanoparticles using K_2PtCl_4

In a typical preparation of aqueous glycolate-protected nanoparticles 10.4 mg (2.5×10^{-5} mol) K_2PtCl_4 was dissolved in 25 mL water along with 9.8 mg sodium glycolate (4 eq.) and heated to approximately 75°C on a water bath. The pH was 7.0. After 90 min the solution had become dark brown indicating the formation of Pt nanoparticles. For aqueous tartrate-protected particles, 11.8 mg potassium tartrate (2 eq.) was used in place of glycolate and the reaction proceeded in a similar manner. See Figure S2.

Hydrogen was also used as the reducing agent to form glycolate-protected Pt nanoparticles. In this case, the solution was held at room temperature while H_2 was bubbled through the solution for 10 min. After about 4 h, the solution had become dark brown, indicating the formation of Pt nanoparticles. See Figure S3.

Stearate-protected nanoparticles using K_2PtCl_4

Stearic acid (0.1 g) was added to 2.0 mL cyclohexane and 3.0 mL isopropanol and allowed to fully dissolve. Then 1.0 mL of 0.02 M K_2PtCl_4 was added. A small amount of isopropanol was added dropwise until the emulsion was no longer turbid. The $PtCl_4^{2-}$ was reduced by addition of 0.1 mL neat hydrazine hydrate. The emulsion turned to dark brown indicating nanoparticle formation. See Figure S4.

Glycine-protected nanoparticles using K_2PtCl_4

pH 10.5 - In a typical preparation of aqueous glycinate-protected nanoparticles, 10.4 mg (2.5×10^{-5} mol) K_2PtCl_4 was dissolved in 2.0 mL water. The solution was brought to 70 °C while stirring before 17.0 mg KI was added, resulting in a dark purple color. The solution was allowed to cool to room temperature, 3.75 mg glycine was added, and the pH was increased to 10.5 by dropwise addition of 1.0 M sodium carbonate, whereupon the solution turned from deep purple to yellow. The solution was then diluted to 25 mL and degassed by the freeze-pump-thaw method three times.

Hydrogen gas was then bubbled through the solution for 5 minutes and the flask remained sealed. Over the course of 10 to 20 minutes the solution turned to deep golden, indicating the formation of Pt nanoparticles, then to a deep violet, then finally resting as a dark brown, non-turbid suspension. See Figure S5.

pH 6 - The above procedure for glycinate-protected nanoparticles was followed except that prior to degassing and introduction of H_2 , the pH was decreased to 6 by addition of 1 M HCl. The initial yellow color achieved under basic conditions was not diminished upon addition of HCl. After H_2 bubbling, the solution turned a bright golden color indicating the formation of Pt nanoparticles. See Figure S6.

pH 3.5 - Another test was performed whereby the above procedure for glycinate-protected nanoparticles was followed, except that prior to degassing and introduction of

H₂, the pH was decreased to 3.5 by addition of 1 M HCl. The initial yellow color achieved under basic conditions was not diminished upon addition of HCl. After H₂ bubbling, the solution turned a dark brown color indicating the formation of Pt nanoparticles. See Figure S7.

N, N –Dimethylglycine-protected nanoparticles using K₂PtCl₄

Into 1 mL water, 4.5 mg (1×10^{-5} mol) potassium tetrachloroplatinate 14.4 mg (8×10^{-5} mol) potassium iodide was added while stirring at 70 °C. The solution became deep violet after about 5 min. The solution was allowed to cool to room temperature and 0.25 mL of 0.1 M solution of *N, N*-dimethylglycine (2.5×10^{-4} mol) was added followed by 4 drops of 1 M NaOH. The solution then became a bright yellow. The solution was then diluted to 25 mL, resulting in a 4.3×10^{-4} M Pt(II) solution with a pH of 10.5. The solution was degassed by 3 freeze- pump-thaw cycles and H₂ was bubbled through it. Within 5 min. the solution turned from yellow to a deep golden indicating the formation of Pt nanoparticles. See Figure S10.

Serine-, Proline-, and Phenylalanine-protected nanoparticles using K₂PtCl₄

In a typical preparation of aqueous serine-protected nanoparticles, 10.4 mg (1×10^{-4} mol) K₂PtCl₄ was dissolved in 25 mL water along with 10.5 mg L-serine (4 eq.) Argon was bubbled through the solution for 15 min followed by hydrogen bubbling for another 15 min. The solution was allowed to sit overnight, after which the solution had become dark brown, indicating the formation of Pt nanoparticles. For aqueous proline-protected particles, 11.5 mg L-proline (4 eq.) was used in place of serine and the reaction proceeded in a similar manner. For aqueous phenylalanine-protected particles, 16.5 mg L-proline (4 eq.) was used in place of serine, and the reaction proceeded in a similar manner. See Figure S9.

Diphenylphosphinoacetate-protected nanoparticles using K₂PtCl₄

Diphenylphosphinoacetic acid (dppa) was prepared following a published procedure.⁴⁶ Four

drops (~0.15 mL) of 1.0 M NaOH were added to 45.0 mg dppa suspended in 2 mL water. The turbid suspension became a clear solution after a few minutes in an ultrasonication bath. Another solution was prepared by dissolving 41.5 mg K_2PtCl_4 (1×10^{-4} mol) in 8 mL water, adding 66.4 mg KI (4×10^{-4} mol), and stirring until the solution became deep violet. The two solutions were then combined. The deep violet color was rapidly replaced by a bright yellow color, which itself gave way to a buff hue after 10 min of stirring. The entire solution was degassed by 3 freeze-pump-thaw cycles and then bubbled with H_2 for 15 min. After approximately 2 h, a black precipitate had deposited onto the bottom of the flask. The supernatant was decanted and the black precipitate was suspended in acetone by ultrasonication bath and sampled for TEM. See Figure S8.

Mercaptoacetate-protected nanoparticles using K_2PtCl_4

A fresh solution of K_2PtCl_4 was prepared by dissolving 10.3 mg (2.5×10^{-6} mol) in 25 mL water. Four equivalents of mercaptoacetic acid (7 mL) were then added, whereupon the solution turned immediately from orange-red to bright yellow. The pH was adjusted to 9 by adding a few drops of 0.1 M NaOH. Since the resulting Pt complex would not be reduced by H_2 , excess $NaBH_4$ was added (1.5 mL of a 0.01 M solution). The solution became dark brown within 1 h. See Figure S8.

Pt nanoparticles using K_2PtI_6 with:

glycine: A 100 mL solution was prepared by dissolving 4.5 mg (6×10^{-5} mol) glycine in distilled water and the pH was adjusted to 10 by addition of 1 M KOH. Potassium hexaiodoplatinate (10.3 mg, 1×10^{-5} mol) was added to the aqueous glycine solution, resulting in a final Pt(IV) concentration of 0.0001 M. The solution was then rapidly filtered through a Nylon syringe filter with a pore size of 0.2 μm into a 250 mL round-bottomed flask. Within 6 min of the initial addition of potassium hexaiodoplatinate and while the solution was still orange in color, the solution was flushed with H_2 for 15 min. After about 2 h the solution had turned from bright yellow to deep golden indicating the formation of Pt nanoparticles. See Figure S11(A).

sarcosine: The above procedure was followed except 5.3 mg (6×10^{-5} mol) sarcosine was used in place of glycine. See Figure S11(B).

N, N-dimethylglycine: The above procedure was followed except 6.2 mg (6×10^{-5} mol) N, N-dimethylglycine was used in place of glycine. See Figure S11(C).

betaine: The above procedure was followed except 7.0 mg (6×10^{-5} mol) betaine was used in place of glycine. See Figure S11(D).

β -alanine: The above procedure was followed except 5.3 mg (6×10^{-5} mol) betaine was used in place of glycine. See Figure S11(E).

no amino acid: The above procedure was followed except that 10.3 g K_2PtI_6 was dissolved in 100 mL KOH solution at pH 10. The solution was flushed with Ar for 15 min before flushing with H_2 for 15 min. No amino acid was used as a protecting agent. See Figure S11(F).

Pt nanoparticles using $\text{H}_2\text{Pt}(\text{OH})_6$ with:

glycine: A solution was prepared by first suspending 15.0 mg $\text{H}_2\text{Pt}(\text{OH})_6$ (5×10^{-5} mol) in 50 mL of water along with 22.5 mg (3×10^{-4} mol). The cloudy suspension was dissolved by dropwise addition of 0.1 M KOH and the solution was then diluted to 100 mL and transferred into a 250 mL round-bottomed flask. The pH was adjusted to 10 upon addition of a few drops of 0.1 M KOH. The flask containing the solution was sealed by rubber septum and the solution was flushed with Ar for 15 min before being flushed with H_2 for 15 min. The flask was left sealed and allowed to stand for 7 days, whereupon the solution began to develop a golden hue. Over the course of the next 24 h, the golden hue darkened indicating that the formation of Pt nanoparticles was complete. See Figure S12(A).

sarcosine: The above procedure was followed except 26.7 mg (3×10^{-4} mol) sarcosine was used in place of glycine. See Figure S12(B).

N, N-dimethylglycine: The above procedure was followed except 30.9 mg (3×10^{-4} mol) N, N-dimethylglycine was used in place of glycine. See Figure S12(C).

betaine: The above procedure was followed except 35.1 mg (3×10^{-4} mol) betaine was used in place of glycine. See Figure S12(D).

β -alanine: The above procedure was followed except 26.7 mg (3×10^{-4} mol) betaine was used in place of glycine. See Figure S12(E).

no amino acid: The above procedure was followed except that a 0.0005 M $K_2Pt(OH)_6$ solution (100 mL) at pH 10 was prepared by suspending $H_2Pt(OH)_6$ in 50 mL water, dissolving by addition of 0.1 M KOH, and adjusting the pH to 10 by further addition of a few drops of KOH solution. The solution was flushed with Ar for 15 min, followed by flushing with H_2 for 15 min. No amino acid was used as a protecting agent. See Figure S12(F).

triflate: The above procedure was followed except that 35.5 mg (3×10^{-4} mol) potassium triflate was used. After flushing the solution with H_2 , the solution became golden within 4 days. See Figure S13(A).

perchlorate: The above procedure was followed except that 41.6 mg (3×10^{-4} mol) potassium perchlorate was used. After flushing the solution with H_2 , the solution became golden within 4 days. See Figure S13(B).

nitrate: The above procedure was followed except that 30.3 mg (3×10^{-4} mol) potassium nitrate was used. After flushing the solution with H_2 , the solution became golden within 7

days. See Figure S13(C).

carbonate: The above procedure was followed except that 41.5 mg (3×10^{-4} mol) potassium carbonate was used. After flushing the solution with H_2 , the solution became golden within 24 h. See Figure S13(D).

Pt nanoparticles using $H_2Pt(OH)_6$ and N_2H_4

A stock solution that was 0.0005 M $K_2Pt(OH)_6$ and 0.003 M dimethylglycine at pH 10 was prepared using $H_2Pt(OH)_6$ and KOH solution. It was used to deliver four 100 mL samples into separate 250 mL round-bottomed flasks. Each sample was then flushed with Ar for 15 min, followed by flushing with H_2 for 15 min. A fresh 0.05 M solution of N_2H_4 was prepared. Reduction of Pt was initiated by addition of 0.2 mL, 0.4 mL, 0.8 mL, and 1.0 mL freshly prepared 0.05 M N_2H_4 , respectively, to the separate samples. All solutions had turned golden indicating the formation of Pt nanoparticles within 24 h. See Figure S14.

Pt Nanoparticles using $H_2Pt(OH)_6$, N_2H_4 , and various anions

A stock solution of 0.005 M $K_2Pt(OH)_6$ was prepared by suspending $H_2Pt(OH)_6$ and adding 1.0 M KOH slowly until the all solids had dissolved. Solutions were prepared of the potassium salts of sulfate, triflate, phosphate (tribasic), chloride, bromide, and carbonate. Each of these solutions was 50 mL and 0.006 M. To each, 10 mL of 0.005 M $K_2Pt(OH)_6$ was added before diluting to 100 mL. The pH of each solution was checked but not adjusted (sulfate = pH 9.8; triflate = pH 10.0; phosphate = pH 11.0; carbonate = pH 10.7; chloride = pH 9.9; bromide = pH 9.8). Hydrogen was flushed through each solution for 15 min before addition of 0.1 mL of freshly prepared 0.5 M N_2H_4 . After being allowed to sit overnight, each solution had become deep golden indicating formation of Pt nanoparticles. See Figure S15.

Pt Nanoparticles using $H_2Pt(OH)_6$ and $NaBH_4$

Hydrogen was flushed for 15 min through 100 mL of 0.0005 M $K_2Pt(OH)_6$ whose pH had

been adjusted to 10 using KOH. Afterwards, 0.1 mL of freshly prepared 0.5 M NaBH₄ was added. The solution became deep golden within 1 h, indicating the formation of Pt nanoparticles. See Figure S16.

B. TEM images of Pt nanoparticle colloids

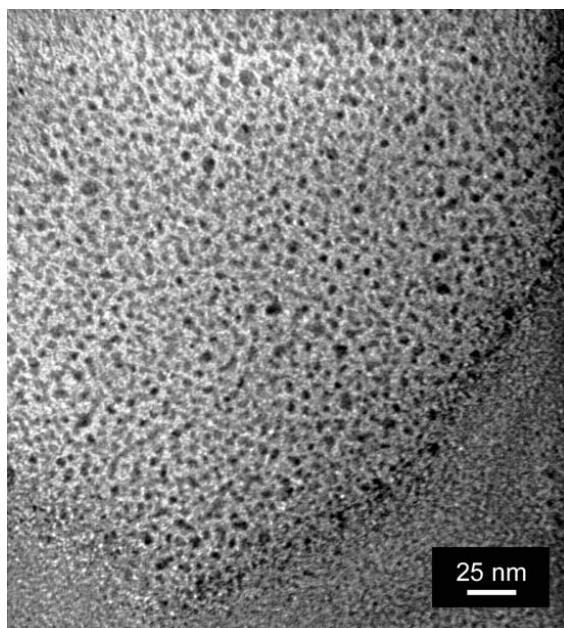


Fig. S1 TEM image of Pt nanoparticles formed using tetrabutylammonium glycolate as capping agent and reducing agent.

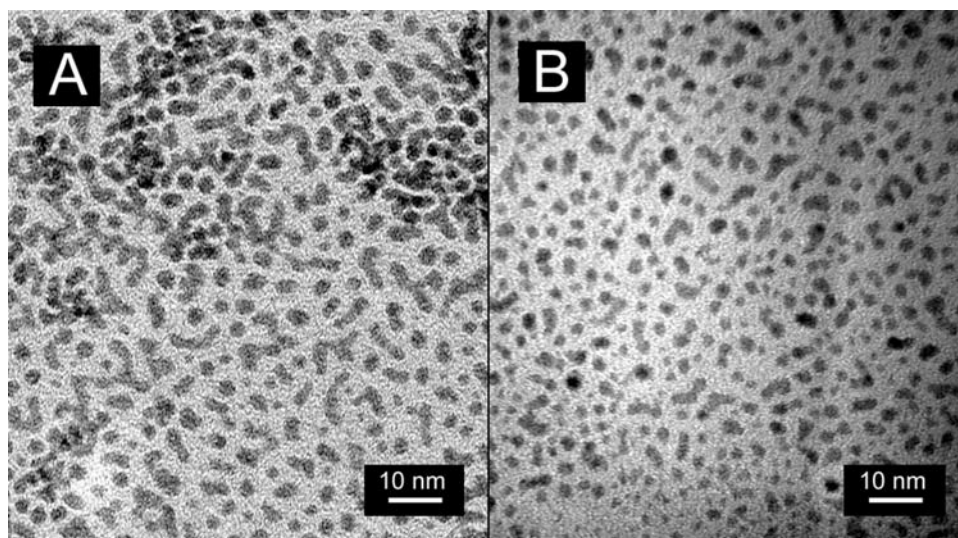


Fig. S2 TEM image of Pt nanoparticles formed by thermal reduction of aqueous $[\text{PtCl}_4]^{2-}$ by glycolate (A) and (B) tartrate salts.

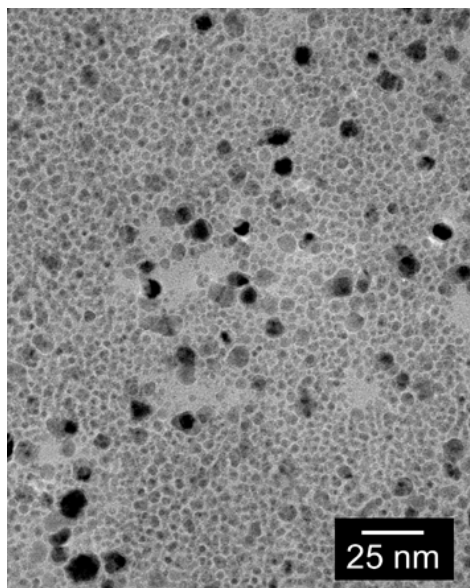


Fig. S3 TEM image of Pt nanoparticles formed by H_2 reduction of $[\text{PtCl}_4]^{2-}$ in the presence of sodium glycolate at pH 7.

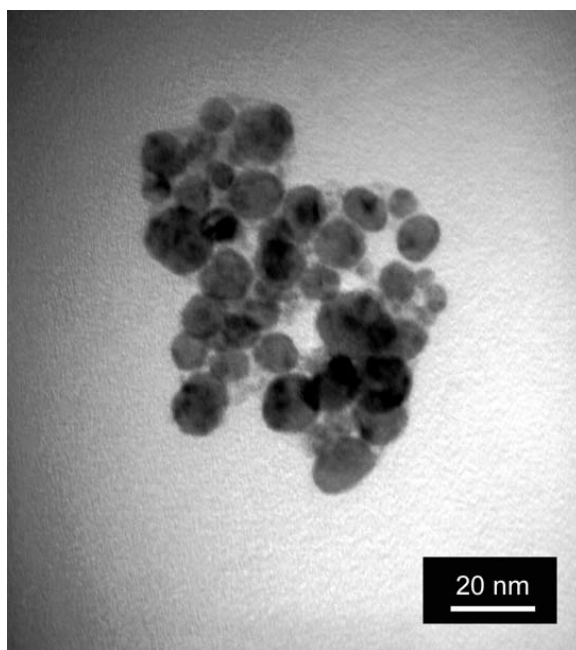


Fig. S4 TEM of spheroidal Pt nanoparticles formed by H_2 reduction of $[\text{PtCl}_4]^{2-}$ in the presence of a stearic acid water-in-oil emulsion.

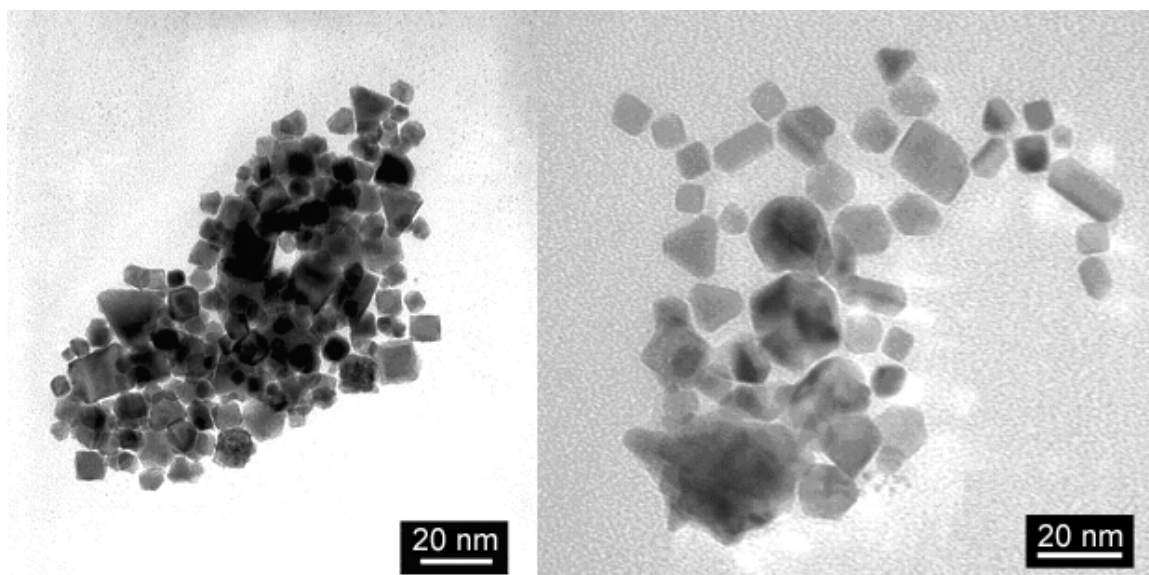


Fig. S5 TEM images of Pt nanoparticles formed by H_2 reduction of $(\text{glycinato})_2\text{PtI}_2$ at pH 10.5.

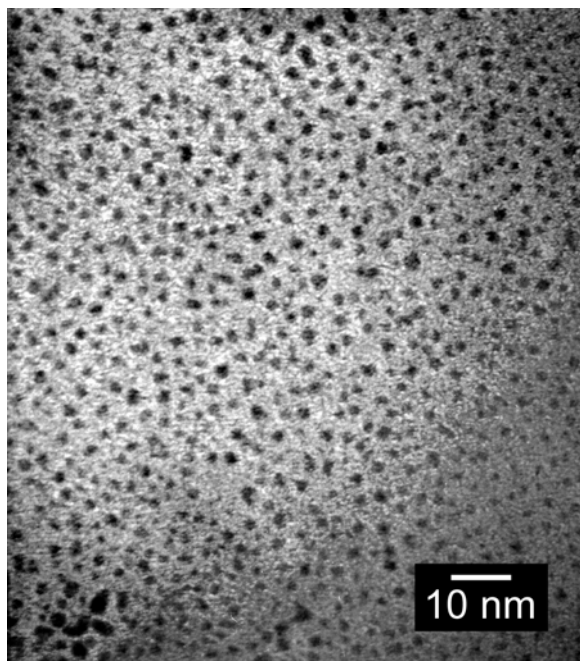


Fig. S6 TEM images of Pt nanoparticles formed by H_2 reduction of $(\text{glycinato})_2\text{PtI}_2$ at pH 6.

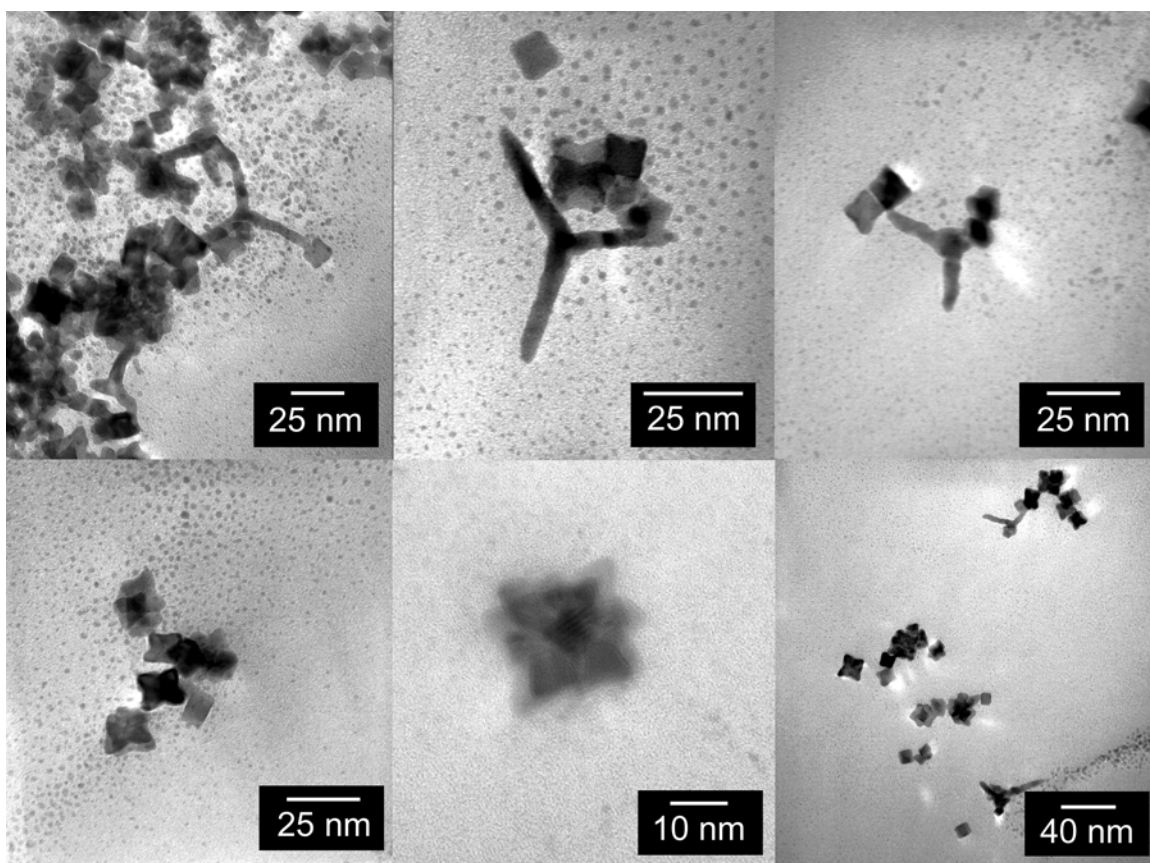


Fig. S7 TEM images of multipodal and multitetrahedral Pt nanoparticles formed by H₂ reduction of (glycinato)₂PtI₂ at pH 3.5.

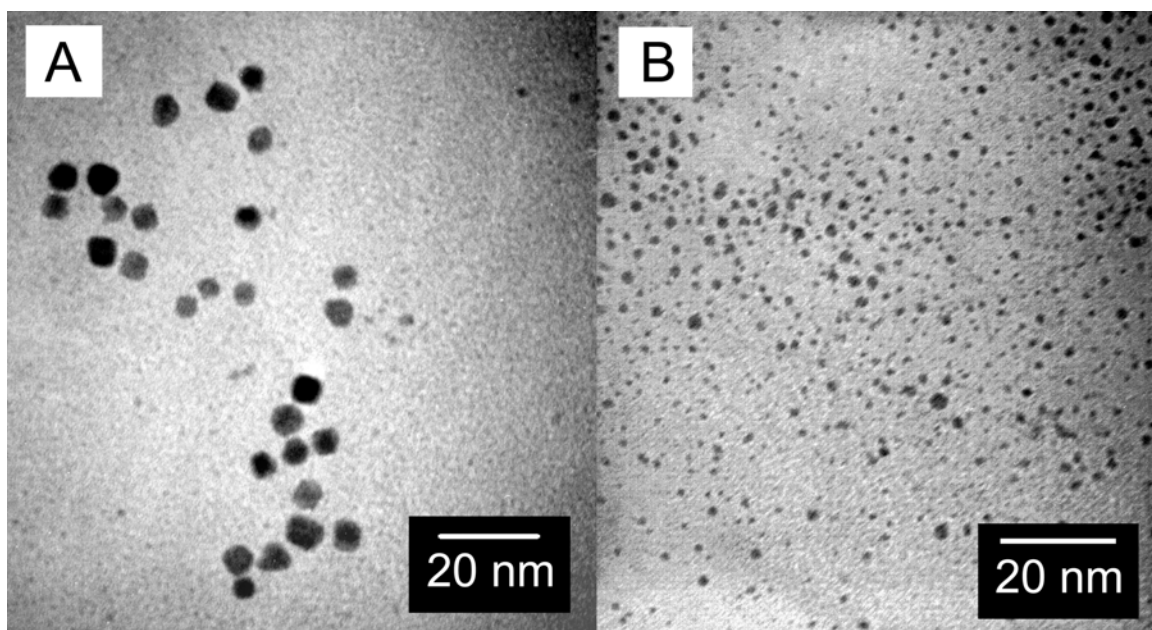


Fig. S8 TEM images of Pt nanoparticles formed in the presence of (A) diphenylphosphinoacetate and (B) mercaptoacetate.

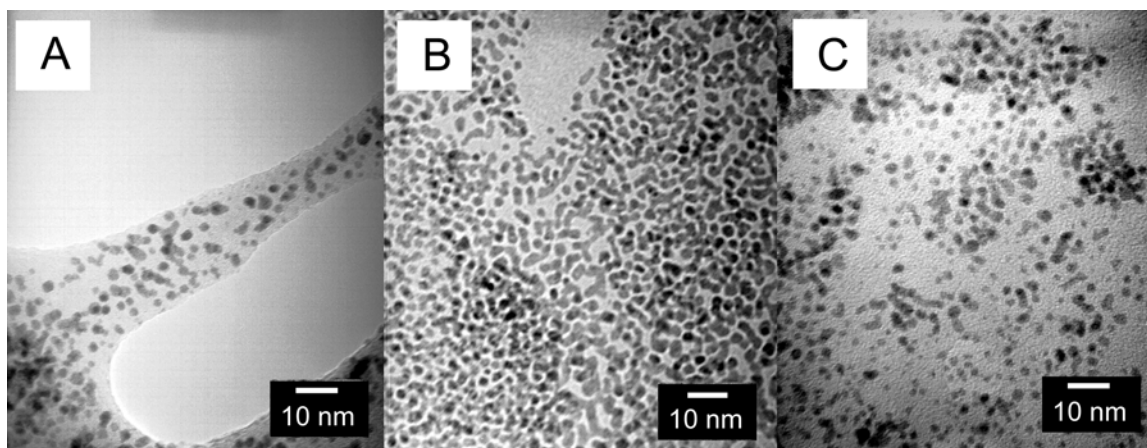


Fig. S9 TEM images of Pt nanoparticles formed in the presence of (A) proline, (B) serine, and (C) phenylalanine.

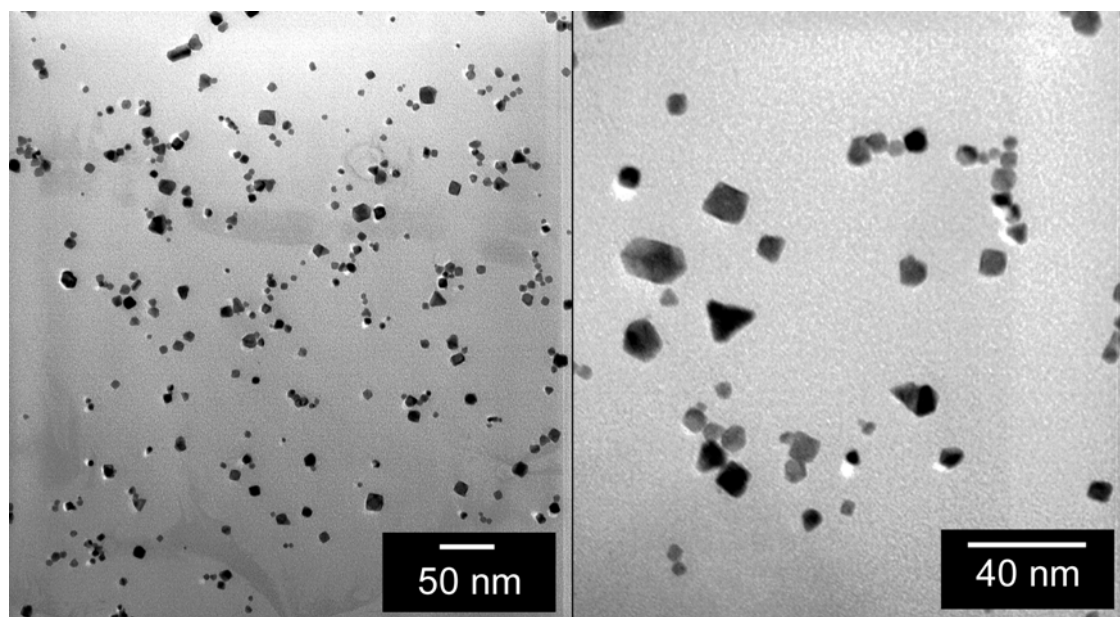


Fig. S10 TEM images of Pt nanoparticles formed by the reduction of $\text{PtI}_2(N, N\text{-dimethylglycine})_2$ at pH 10.5.

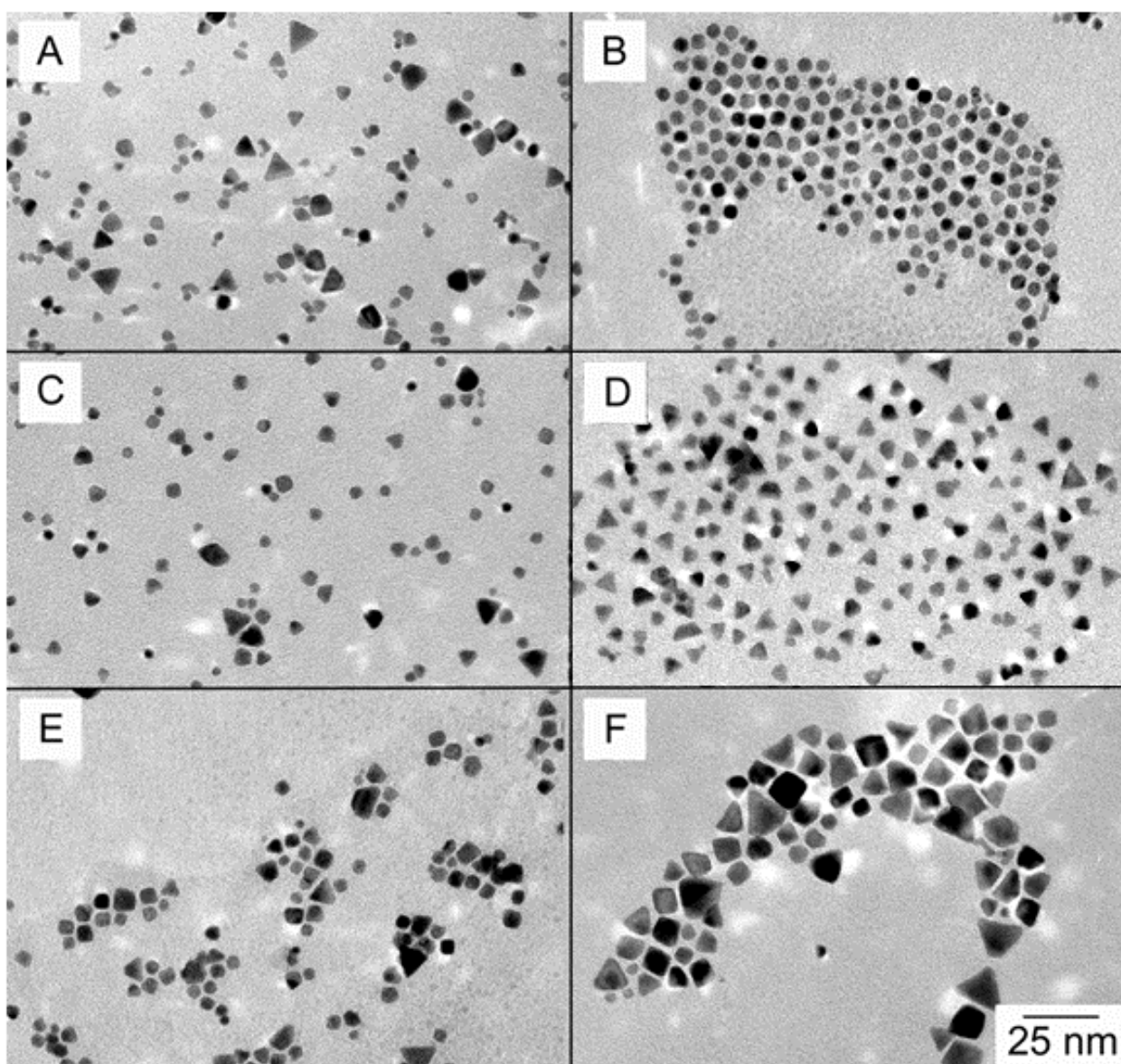


Fig. S11 TEM images of tetrahedral Pt nanoparticles formed by H_2 reduction of K_2PtI_6 in the presence of (A) glycine, (B) sarcosine, (C) dimethylglycine, (D) betaine, (E) β -alanine, and (F) no amino acid. The scale bar applies to every image.

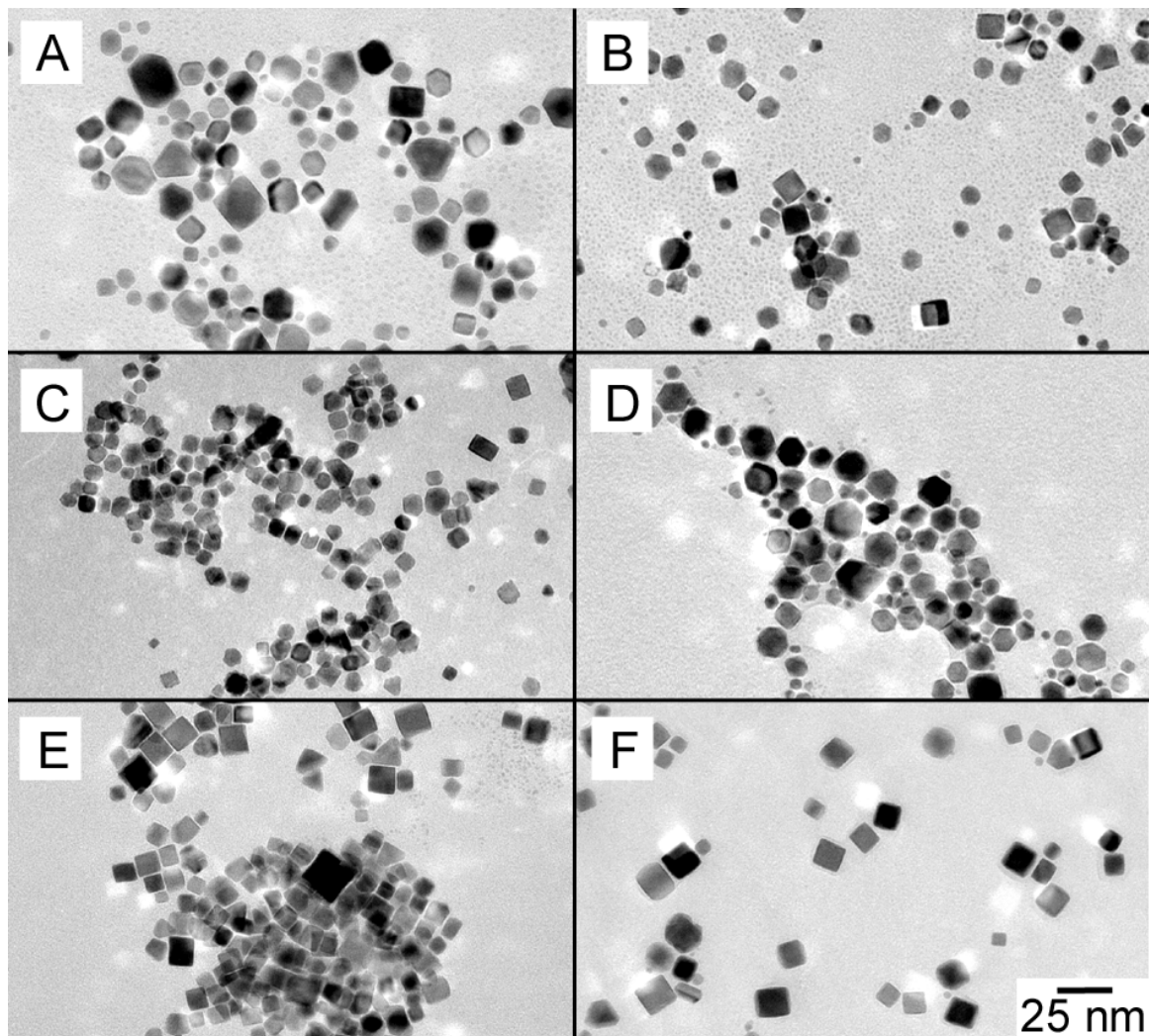


Fig. S12 The appearance of Pt nanoparticles formed by the H₂ reduction of [Pt(OH)₆]²⁻ at pH 10 in the presence of 6 eq. of (A) glycine, (B) sarcosine, (C) N, N-dimethylglycine, (D) betaine, (E) β-alanine, and (F) no amino acid.

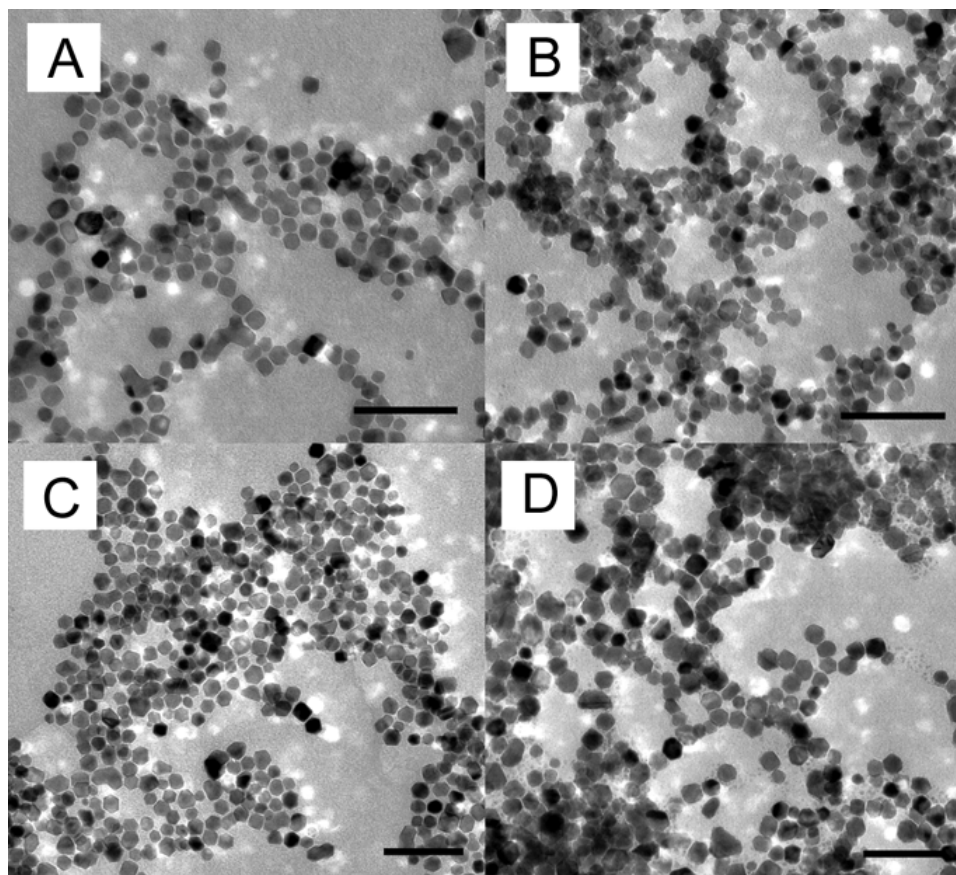


Fig. S13 TEM images of Pt nanoparticles formed by H_2 reduction of $[\text{Pt}(\text{OH})_6]^{2-}$ in the presence of 6 eq. of (A) triflate, (B) nitrate, (C) perchlorate, and (D) carbonate ions (Scale bars=25 nm).

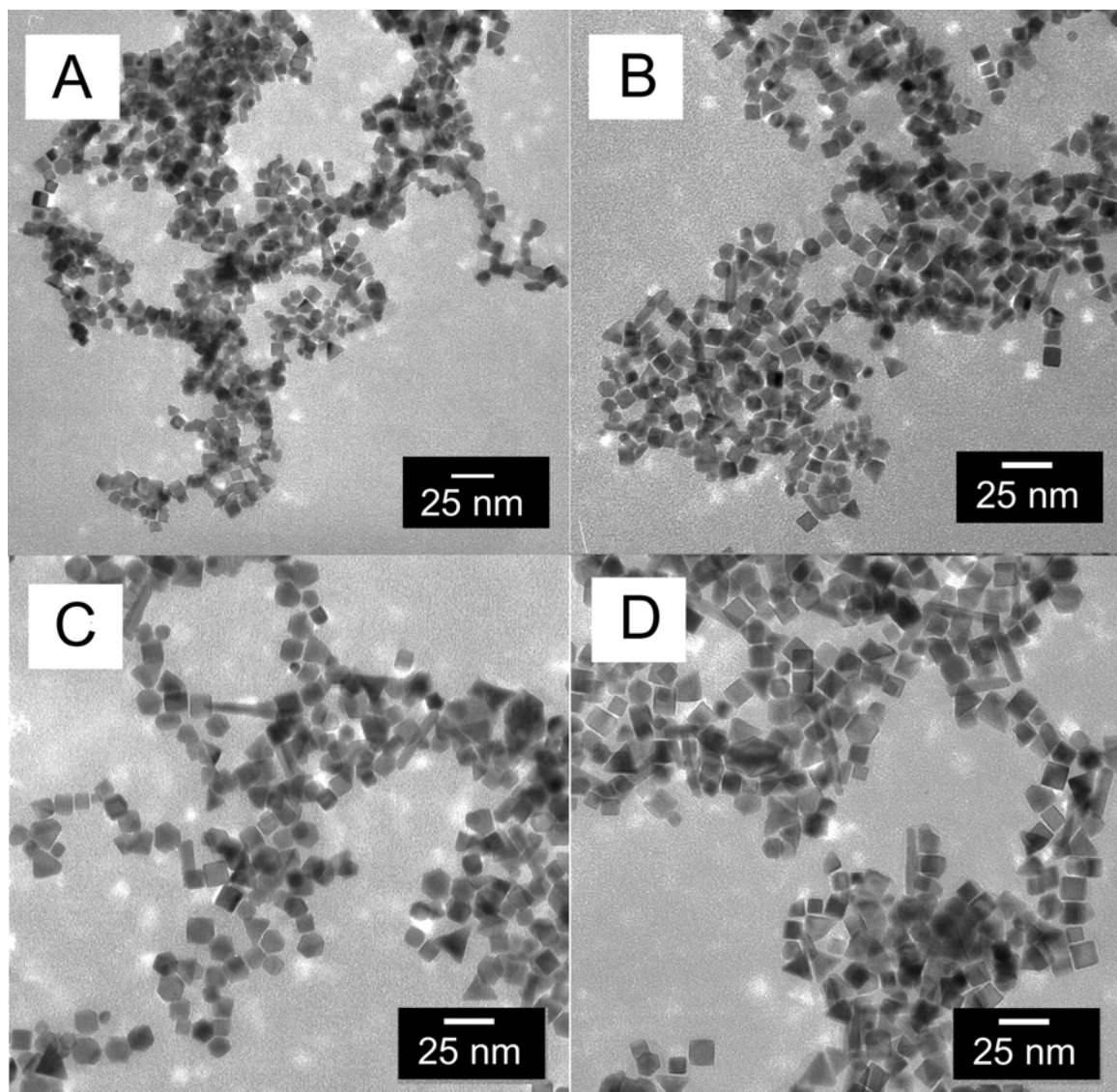


Fig. S14 TEM images showing the appearance of Pt nanoparticles formed by reduction of $[\text{Pt}(\text{OH})_6]^{2-}$ using (A) 0.2 eq. (B) 0.4 eq. (C) 0.8 eq. and (D) 1.0 eq. hydrazine in the presence of dimethylglycine. Note the increase in the number of tetrahedra and nanorods with increasing hydrazine concentration.

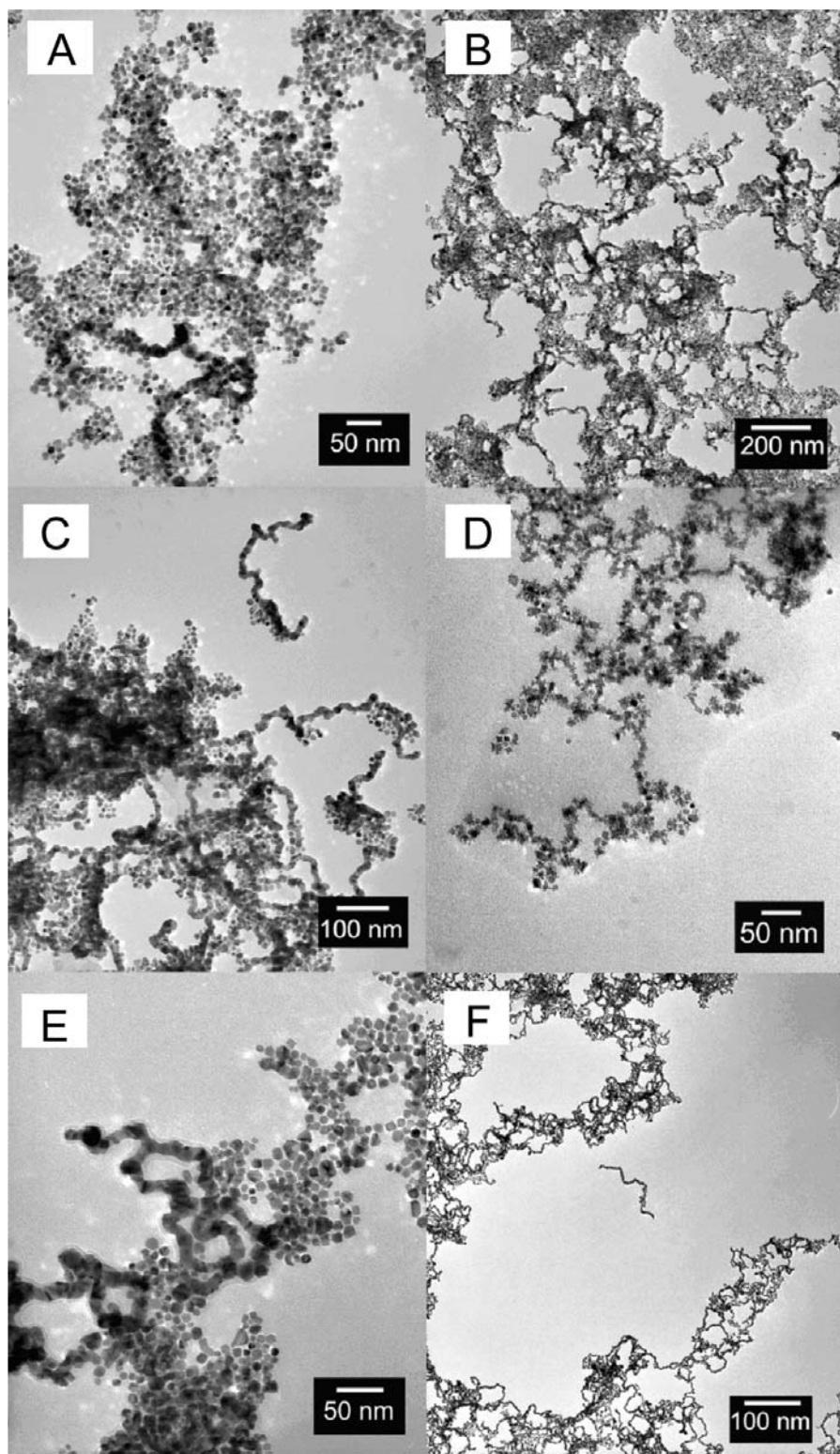


Fig. S15 TEM images showing the appearance of Pt nanoparticles formed by reduction of $[\text{Pt}(\text{OH})_6]^{2-}$ by hydrazine in the presence of 6 eq. of (A) chloride, (B) bromide, (C) carbonate, (D) phosphate, (E) sulfate, and (F) triflate.

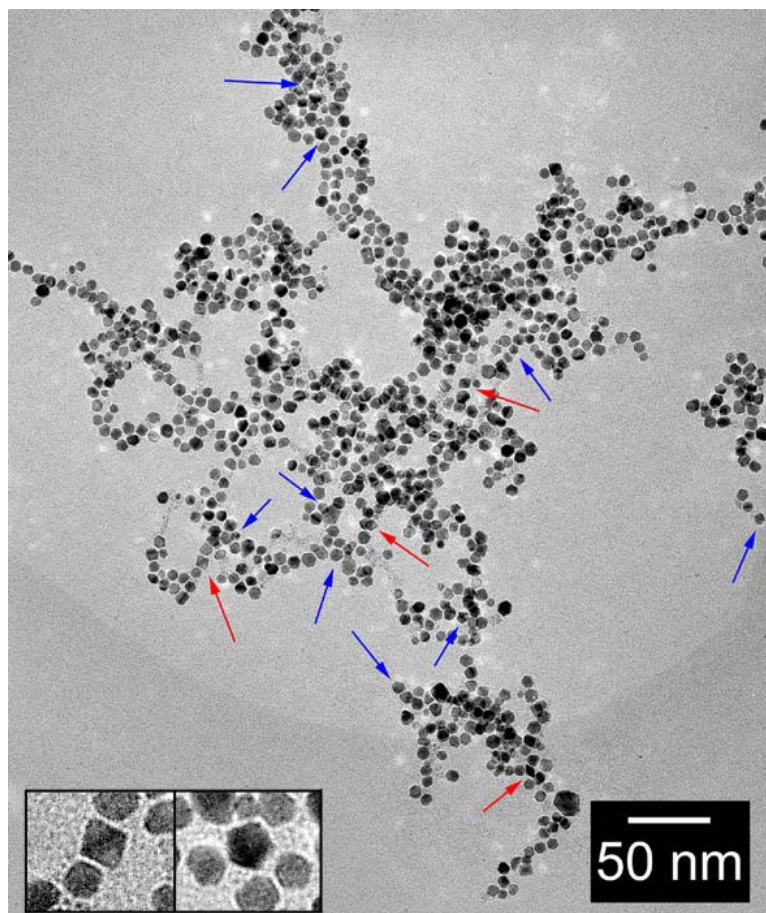


Fig. S16 TEM image showing the appearance of Pt nanoparticles formed by reduction of $[\text{Pt}(\text{OH})_6]^{2-}$ by borohydride. The locations of octahedra are marked with red arrows. Blue arrows mark the locations of decahedra. Representatives of each shape are shown (inset).