SUPPORTING INFORMATION

A Systematic Study of the Synthesis of Silver Nanoplates: Is Citrate a "Magic" Reagent?

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Experimental Sections

Chemicals. Hydrogen peroxide (H_2O_2, 30 wt-%), acetic acid (glacial), sodium hydroxide, and sodium potassium tartrate were purchased from Fisher Scientific. Silver nitrate ($AgNO_3$, 99+%), sodium borohydride ($NaBH_4$, 99%), ethylene glycol (EG), sodium citrate tribasic dihydrate (TSC, 99%), tricarballylic acid (99%), and L-ascorbic acid were obtained from Sigma-Aldrich. Polyvinylpyrrolidone (PVP, M_w ~ 29,000) was purchased from Fluka. Malonic acid disodium salt monohydrate (99%), succinic acid disodium anhydrous (99%), glutaric acid (99%), oxalic acid (98%), DL-isocitric acid trisodium hydrate (98%), 1,3,5-benzenetricarboxyllic acid (98%), pimelic acid (98%) and polyethylene glycol (PEG, Mw ~ 3500) were purchased from Acros Organics. Adipic acid disodium salt was purchased from TCI America. Diethylene glycol (DEG) was purchased from Alfa Aesar. All chemicals were used as received without further treatment.

Synthesis of Ag nanoplates Typically, the total volume of the reaction solution is fixed at 25.00 mL. In 24.14 mL of pure water, an aqueous solution of silver nitrate (0.05 M, 50 μL), trisodium citrate (75 mM, 0.5 mL), and H_2O_2 (30 wt %, 60 μL) were combined and vigorously stirred at

room temperature in air. Sodium borohydride ($NaBH_4$, 100 mM, 250 μL) is rapidly injected into this mixture to get the nanoplates. After ~3 min, the colloid turns to a deep-yellow color, due to the formation of small silver nanoparticles. Within the next several minutes, the morphology continues to change from particles to nanoplates accompanied by the solution color changing from yellow to blue. For the other specific conditions, e.g., different surfactants or concentrations, the synthetic strategies are described in the Caption of each figure in Supporting Information.

Synthesis of Ag nanowires. Ag nanowires are prepared by a modified polyol process developed by Xia and co-workers (Y. Sun, B. Mayers, T. Herricks, Y. Xia, *Nano Letters* **2003**, *3*, 955.), in which $AgNO_3$ was reduced by EG in the presence of Pt seeds and PVP. In a typical process, 15 mL of EG was heated at 170 ^oC for 2 hours under magnetic stirring. 4.5 mL EG solution of 0.1 mM K_2PtCl_6 was then rapidly injected into the EG solution, which became light brown in several seconds, confirming the formation of Pt seeds. 5 min later, 18 mL EG solution of a mixture of $AgNO_3$ (0.05 M) and PVP (Mw ~ 40,000, 0.1 M) was added dropwise to the seeds solution through a syringe pump at a rate of 0.5 mL/min. This reaction mixture was then heated at 170 ^oC for another 40 min to ensure the complete reduction of $AgNO_3$. The as-obtained product is then washed with ethanol for three times and D.I. H_2O for twice, and finally dispersed in 40 mL of D.I. H_2O.

Synthesis of Ag nanoplates from Ag nanowires Typically, 0.1 mL of Ag nanowires (out of 40 mL) was dispersed in 24.25 mL of H_2O first, followed by mixing trisodium citrate (75 mM, 0.3 mL), and hydrogen peroxide (30 wt. %, 100 μL) were combined and vigorously stirred at room temperature in air. 10 min later, sodium borohydride ($NaBH_4$, 100 mM, 250 μL) is rapidly injected into this mixture, generating a pale yellow colloidal solution. After ~3 min, the colloid turns to a deep-yellow color, due to the formation of small silver nanoparticles. Within the next

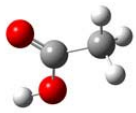
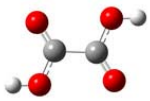
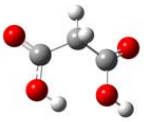
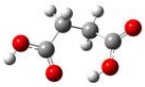
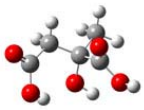
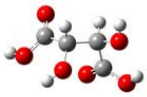
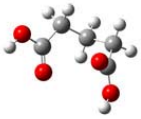
several seconds, the morphology continues to change from particles to nanoplates accompanied by the solution color changing from yellow to blue.

Synthesis of Ag nanoparticles In 24.1 mL of pure water, an aqueous solution of silver nitrate (0.05 M, 50 μL), trisodium citrate (75 mM, 0.5 mL), poly (vinylpyrrolidone) (PVP, weight-average molecular weight Mw ~ 29, 000 g/mol, 17.5 mM, 0.1 mL) were combined and vigorously stirred at room temperature in air. Sodium borohydride ($NaBH_4$, 100 mM, 250 μL) is rapidly injected into this mixture to get the nanoparticles.

Synthesis of Ag plates from Ag nanoparticles To the as-obtained yellow Ag sol, hydrogen peroxide (30 wt. %, 60 μL) is rapidly injected. Sodium borohydride ($NaBH_4$, 100 mM, 250 μL) was then quickly injected to get the final product.

Characterization The morphology of Ag nanoparticles was characterized by using a Tecnai T12 transmission electron microscope (TEM). The measurement of optical property was conducted by using a Varian Cary 50 UV/Vis spectrophotometer (190 nm – 1100 nm). A probe-type Ocean Optics HR2000CG-UV-NIR spectrometer was used to measure the UV-Vis spectra of the reaction system to get the real-time spectra change during the synthesis of silver nanoplates.

Computational method The molecules were built by using GaussView 4.1. The geometries were then optimized at the Hartree-Fork level with 6-31G(d) basis set by Gaussian 03W.

Name	Structure	Distance between two nearest carboxylic groups (Å)	Yield of plates
Acetic acid		N/A	~ 0%
Oxalic acid		2.69	~ 0%
Malonic acid		2.68	~80%
Succinic acid		2.78	~100%
Citramalic acid		3.82	~100%
Tartaric acid		3.26	~80%
Glutaric acid		3.26	~50%
Adipic acid		2.87	~20%

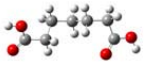
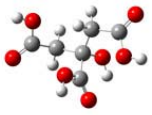
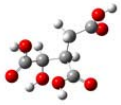
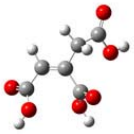
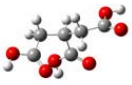
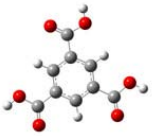
Pimelic acid		6.62	~ 0%
Citric acid		3.12	~100%
Isocitric acid		3.09	~90%
cis-Aconitic acid		2.82	~90%
Tricarballylic acid		3.18	~85%
Trimesic Acid		4.76	~ 0%

Table S1. The 3D structures of carboxyl compounds with different numbers of carboxylic groups and chain lengths that have been used as the capping agent to prepare silver nanoplates.

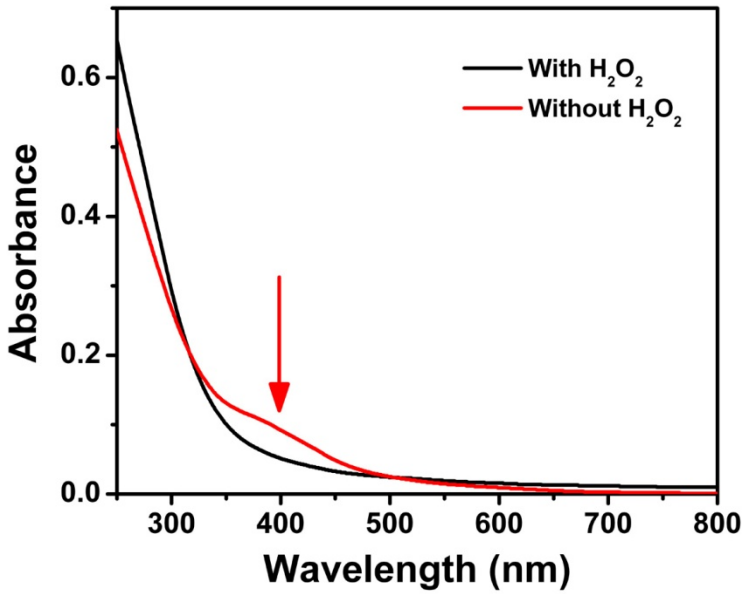


Figure S1 The UV/Vis spectra showing the influence of H_2O_2 in the initial stage by comparing the spectra obtained in the absence (red) and in the presence (black) of H_2O_2, respectively.

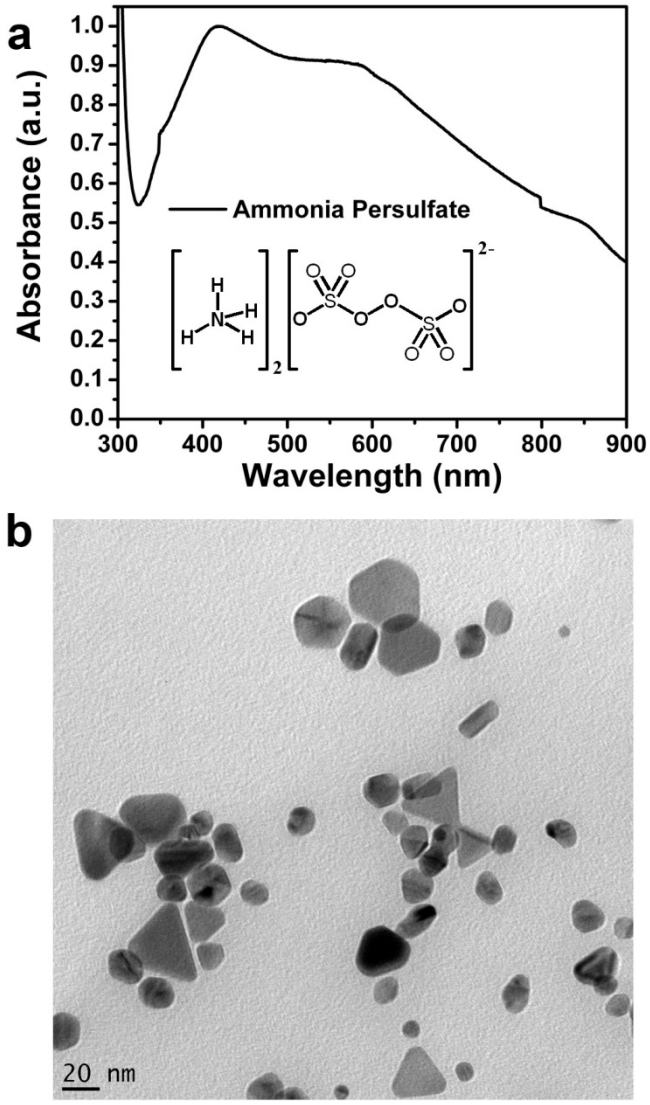


Figure S2 The UV-vis spectrum (a) and TEM image (b) of a typical sample prepared by substituting ammonium persulfate ($(NH_4)_2S_2O_8$, APS) for $NaBH_4$.

*Synthesis of silver nanoplates by using **APS.*** Typically, the total volume of the reaction solution is fixed at 25.00 mL. In 24.24 mL of pure water, an aqueous solution of silver nitrate (0.05 M, 50 μL), trisodium citrate (75 mM, 0.5 mL), poly (vinylpyrrolidone) (PVP, weight-average molecular weight Mw ~ 29, 000 g/mol, 17.5 mM, 0.1 mL), and APS (0.5 M, 1 mL) were combined and vigorously stirred at room temperature in air. Sodium borohydride ($NaBH_4$, 100 mM, 50 μL) is rapidly injected into this mixture to get the nanoplates.

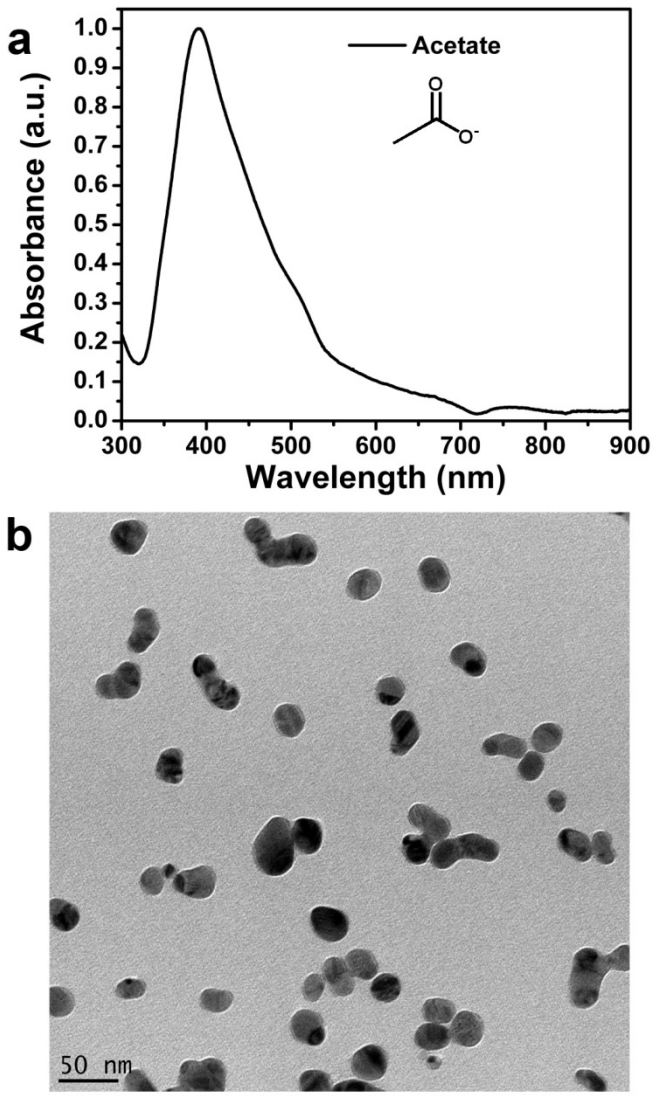


Figure S3 The UV-vis spectrum (a) and TEM image (b) of a typical sample prepared by substituting sodium acetate for trisodium citrate.

*Synthesis of silver nanoplates by using **acetate*** Typically, the total volume of the reaction solution is fixed at 25.00 mL. In 24.19 mL of pure water, an aqueous solution of silver nitrate (0.05 M, 50 μL), sodium acetate (75 mM, 0.5 mL), poly (vinylpyrrolidone) (PVP, weight-average molecular weight Mw ~ 29, 000 g/mol, 17.5 mM, 0.1 mL), and hydrogen peroxide (30 wt. %, 60 μL) were combined and vigorously stirred at room temperature in air. Sodium borohydride ($NaBH_4$, 100 mM, 100 μL) is rapidly injected into this mixture to get the final product.

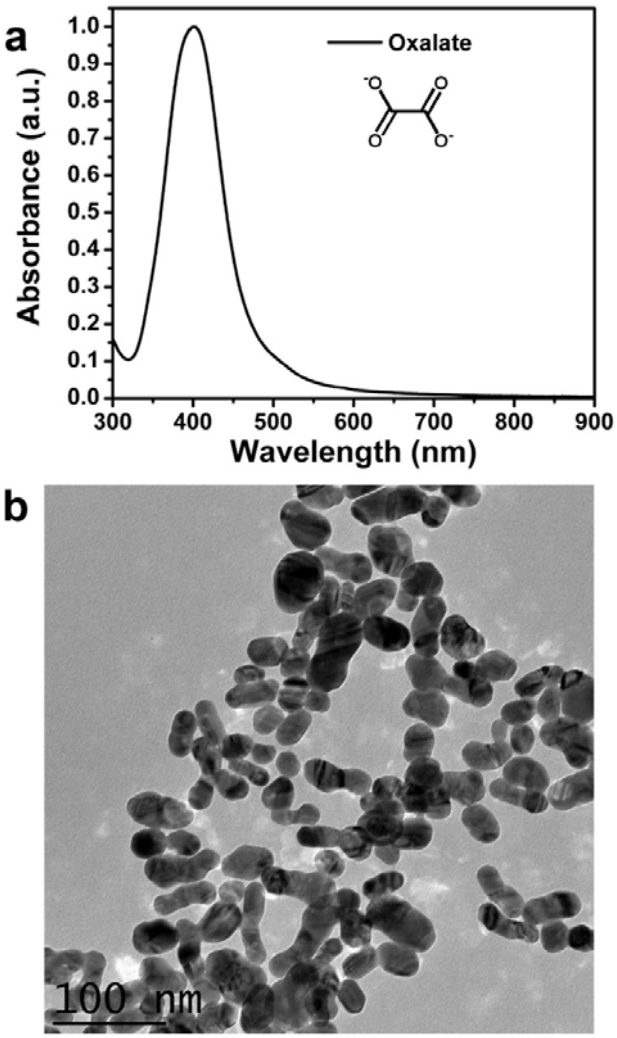


Figure S4 The UV-vis spectrum (a) and TEM image (b) of a typical sample prepared by substituting disodium oxalate for trisodium citrate.

Synthesis of silver nanoplates by using ***oxalate*** Typically, the total volume of the reaction solution is fixed at 25.00 mL. In 24.19 mL of pure water, an aqueous solution of silver nitrate (0.05 M, 50 μL), disodium oxalate (75 mM, 0.5 mL), poly (vinyl pyrrolidone) (PVP, weight-average molecular weight Mw ~ 29, 000 g/mol, 17.5 mM, 0.1 mL), and hydrogen peroxide (30 wt. %, 60 μL) were combined and vigorously stirred at room temperature in air. Sodium borohydride ($NaBH_4$, 100 mM, 100 μL) is rapidly injected into this mixture to get the final product.

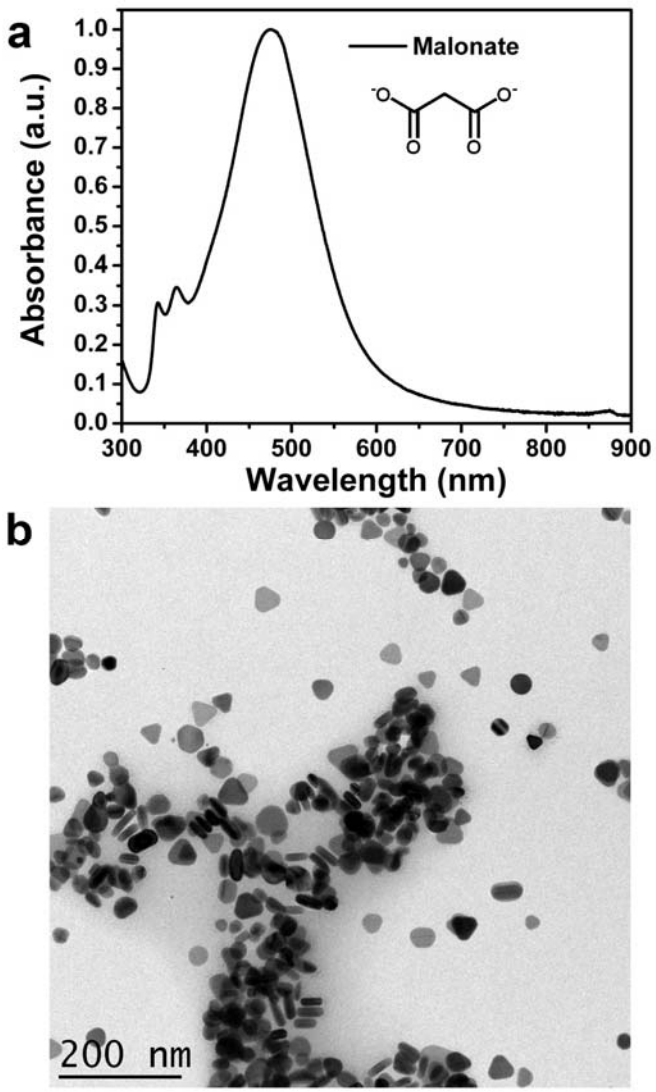


Figure S5 The UV-vis spectrum (a) and TEM image (b) of a typical sample prepared by substituting disodium malonate for trisodium citrate.

*Synthesis of silver nanoplates by using **malonate*** Typically, the total volume of the reaction solution is fixed at 25.00 mL. In 24.24 mL of pure water, an aqueous solution of silver nitrate (0.05 M, 50 μL), disodium malonate (75 mM, 0.5 mL), poly (vinylpyrrolidone) (PVP, weight-average molecular weight Mw ~ 29, 000 g/mol, 17.5 mM, 0.1 mL), and hydrogen peroxide (30 wt. %, 60 μL) were combined and vigorously stirred at room temperature in air. Sodium borohydride ($NaBH_4$, 100 mM, 50 μL) is rapidly injected into this mixture to get the nanoplates.

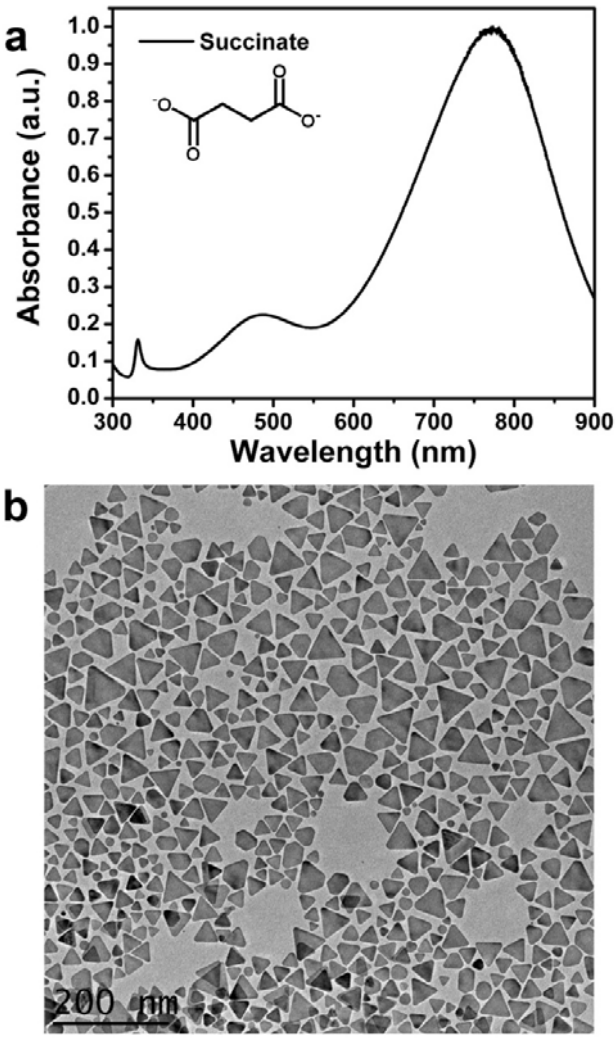


Figure S6 The UV-vis spectrum (a) and TEM image (b) of a typical sample prepared by substituting disodium succinate for trisodium citrate.

Synthesis of silver nanoplates by using ***succinate*** Typically, the total volume of the reaction solution is fixed at 25.00 mL. In 24.24 mL of pure water, an aqueous solution of silver nitrate (0.05 M, 50 μL), disodium succinate (75 mM, 0.5 mL), poly (vinylpyrrolidone) (PVP, weight-average molecular weight Mw ~ 29, 000 g/mol, 17.5 mM, 0.1 mL), and hydrogen peroxide (30 wt. %, 30 μL) were combined and vigorously stirred at room temperature in air. Sodium borohydride ($NaBH_4$, 100 mM, 50 μL) is rapidly injected into this mixture to get the nanoplates.

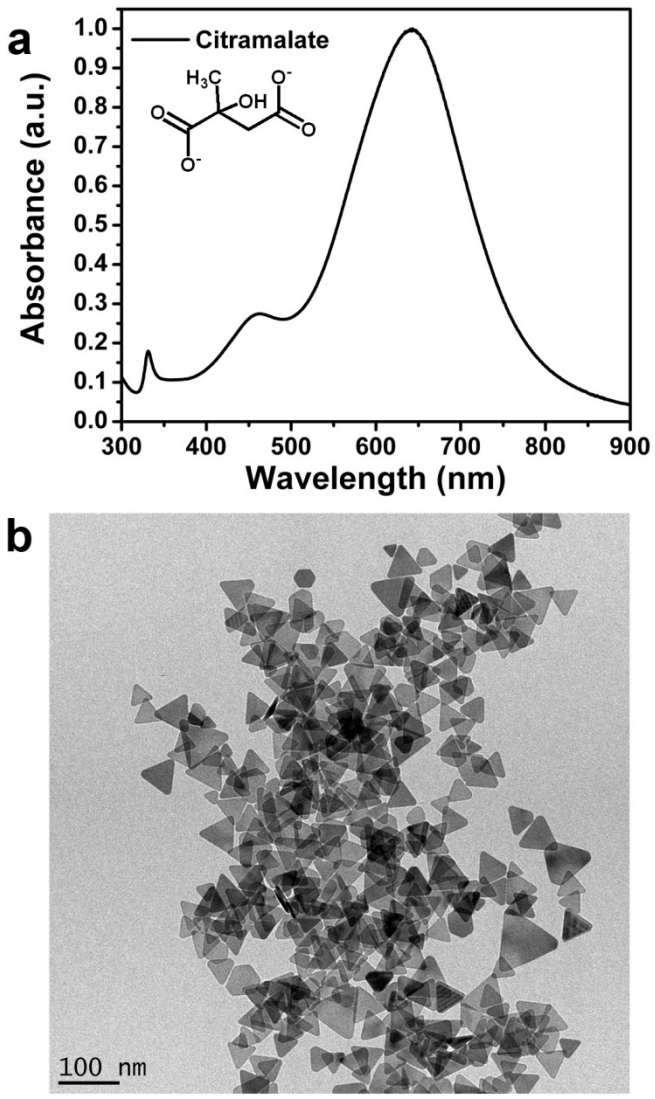


Figure S7 The UV-vis spectrum (a) and TEM image (b) of a typical sample prepared by substituting disodium citramalate for trisodium citrate.

Synthesis of silver nanoplates by using ***citramalate*** Typically, the total volume of the reaction solution is fixed at 25.00 mL. In 24.24 mL of pure water, an aqueous solution of silver nitrate (0.05 M, 50 μL), disodium citramalate (75 mM, 0.5 mL), poly (vinylpyrrolidone) (PVP, weight-average molecular weight Mw ~ 29, 000 g/mol, 17.5 mM, 0.1 mL), and hydrogen peroxide (30 wt. %, 60 μL) were combined and vigorously stirred at room temperature in air. Sodium borohydride ($NaBH_4$, 100 mM, 50 μL) is rapidly injected into this mixture to get the nanoplates.

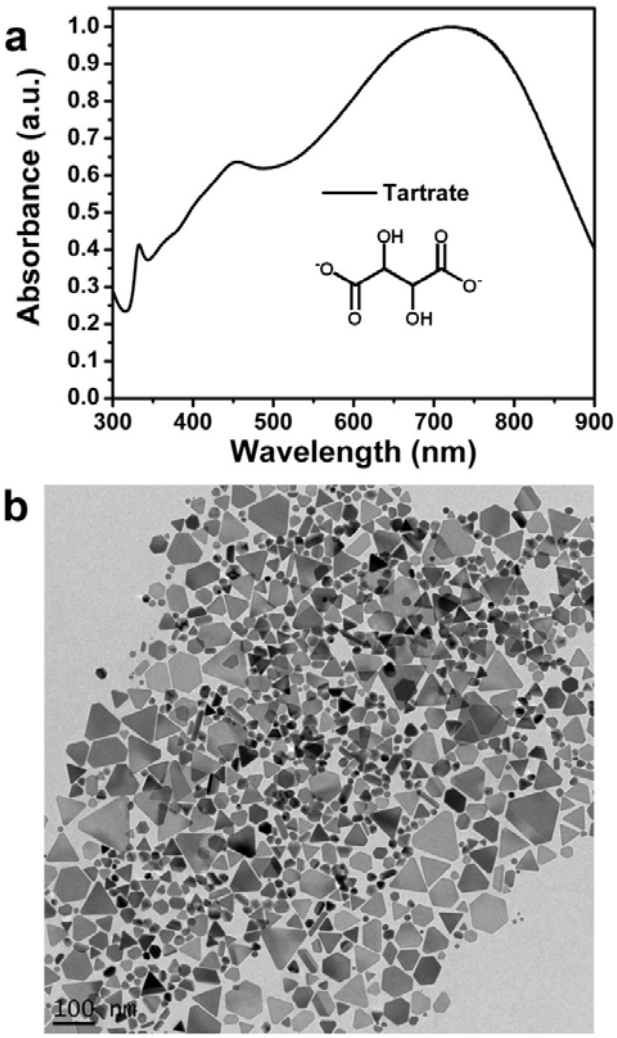


Figure S8 The UV-vis spectrum (a) and TEM image (b) of a typical sample prepared by substituting disodium tartrate for trisodium citrate.

*Synthesis of silver nanoplates by using **tartrate*** Typically, the total volume of the reaction solution is fixed at 25.00 mL. In 24.24 mL of pure water, an aqueous solution of silver nitrate (0.05 M, 50 μL), sodium potassium tartrate (75 mM, 0.5 mL), poly (vinylpyrrolidone) (PVP, weight-average molecular weight Mw ~ 29, 000 g/mol, 17.5 mM, 0.1 mL), and hydrogen peroxide (30 wt. %, 30 μL) were combined and vigorously stirred at room temperature in air. Sodium borohydride ($NaBH_4$, 100 mM, 50 μL) is rapidly injected into this mixture to get the nanoplates.

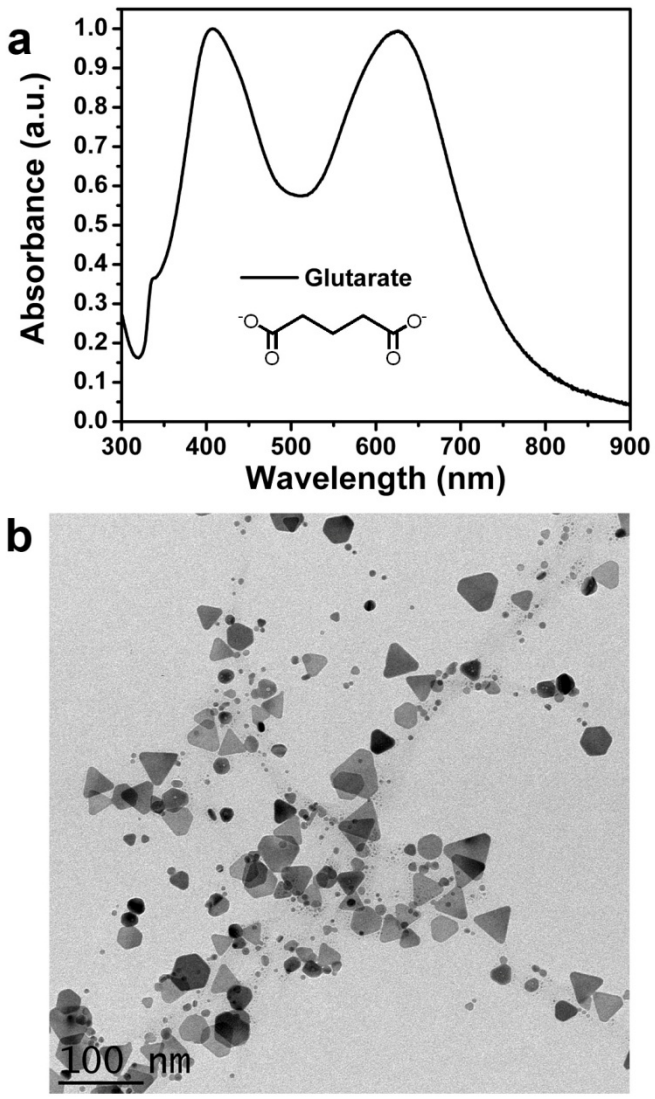


Figure S9 The UV-vis spectrum (a) and TEM image (b) of a typical sample prepared by substituting disodium glutarate for trisodium citrate.

*Synthesis of silver nanoplates by using **glutarate*** Typically, the total volume of the reaction solution is fixed at 25.00 mL. In 24.19 mL of pure water, an aqueous solution of silver nitrate (0.05 M, 50 μL), disodium glutarate (75 mM, 0.5 mL), poly (vinylpyrrolidone) (PVP, weight-average molecular weight Mw ~ 29, 000 g/mol, 17.5 mM, 0.1 mL), and hydrogen peroxide (30 wt. %, 60 μL) were combined and vigorously stirred at room temperature in air. Sodium borohydride ($NaBH_4$, 100 mM, 100 μL) is rapidly injected into this mixture to get the nanoplates.

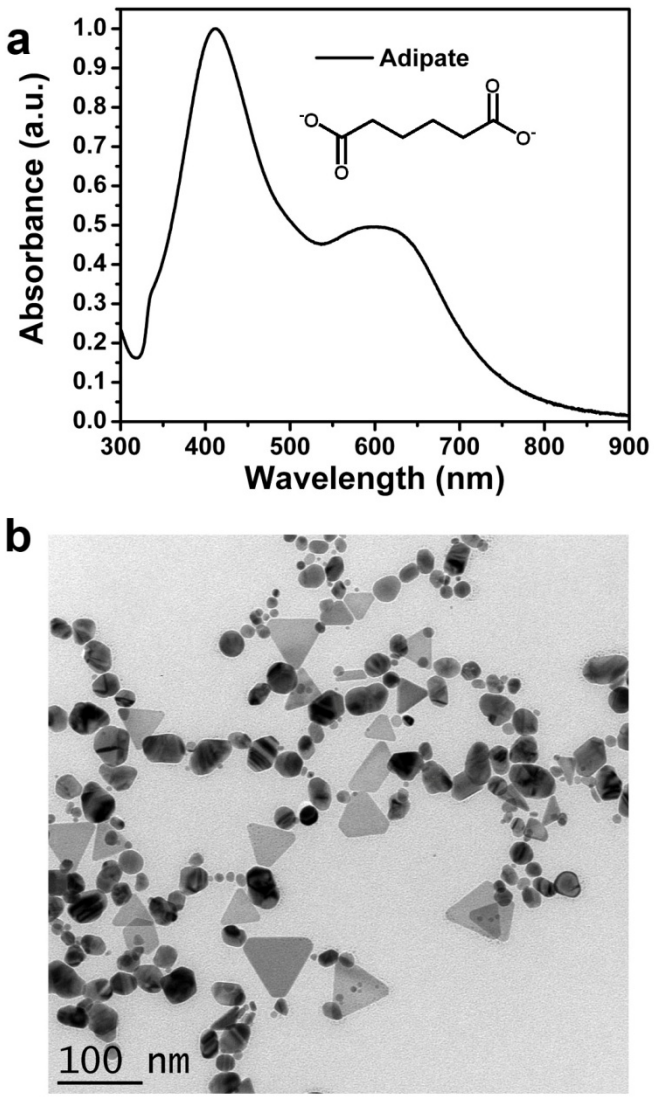


Figure S10 The UV-vis spectrum (a) and TEM image (b) of a typical sample prepared by substituting disodium adipate for trisodium citrate.

*Synthesis of silver nanoplates by using **adipate*** Typically, the total volume of the reaction solution is fixed at 25.00 mL. In 24.24 mL of pure water, an aqueous solution of silver nitrate (0.05 M, 50 μL), disodium adipate (75 mM, 0.5 mL), poly (vinylpyrrolidone) (PVP, weight-average molecular weight Mw ~ 29, 000 g/mol, 17.5 mM, 0.1 mL), and hydrogen peroxide (30 wt. %, 60 μL) were combined and vigorously stirred at room temperature in air. Sodium borohydride ($NaBH_4$, 100 mM, 50 μL) is rapidly injected into this mixture to get the nanoplates.

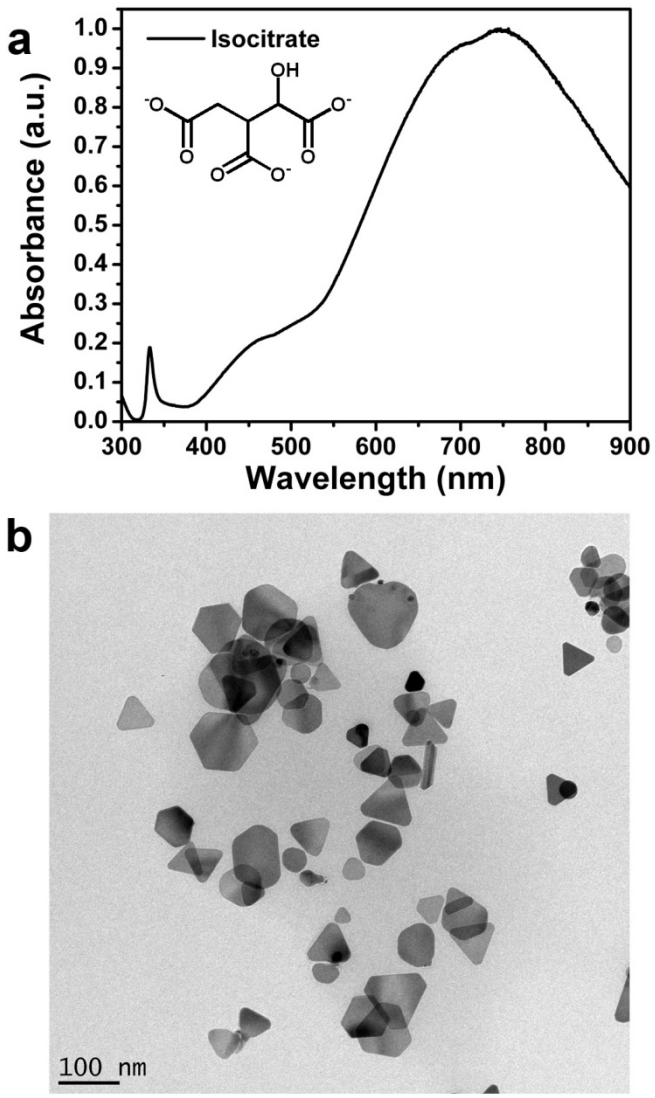


Figure S11 The UV-vis spectrum (a) and TEM image (b) of a typical sample prepared by substituting trisodium isocitrate for trisodium citrate.

Synthesis of silver nanoplates by using ***isocitrate*** Typically, the total volume of the reaction solution is fixed at 25.00 mL. In 24.19 mL of pure water, an aqueous solution of silver nitrate (0.05 M, 50 μL), trisodium isocitrate (75 mM, 0.5 mL), and hydrogen peroxide (30 wt. %, 30 μL) were combined and vigorously stirred at room temperature in air. Sodium borohydride ($NaBH_4$, 100 mM, 100 μL) is rapidly injected into this mixture to get the nanoplates.

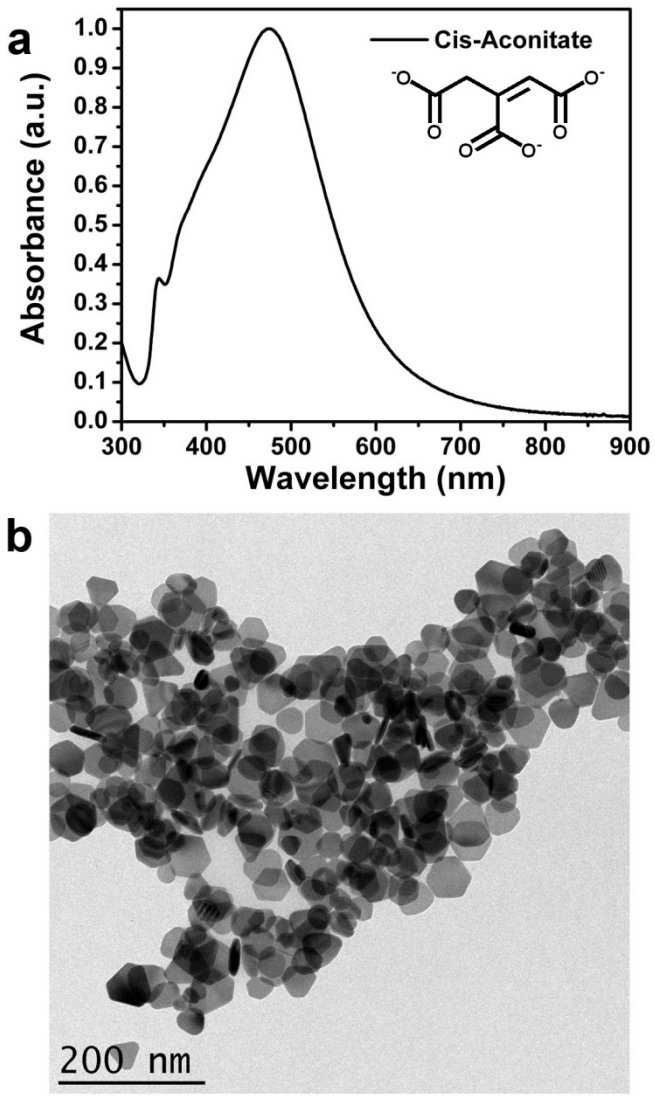


Figure S12 The UV-vis spectrum (a) and TEM image (b) of a typical sample prepared by substituting trisodium cis-aconitate for trisodium citrate.

*Synthesis of silver nanoplates by using **cis-aconitate*** Typically, the total volume of the reaction solution is fixed at 25.00 mL. In 24.19 mL of pure water, an aqueous solution of silver nitrate (0.05 M, 50 μL), trisodium cis-aconitate (75 mM, 0.5 mL), poly (vinylpyrrolidone) (PVP, weight-average molecular weight Mw ~ 29, 000 g/mol, 17.5 mM, 0.1 mL), and hydrogen peroxide (30 wt. %, 30 μL) were combined and vigorously stirred at room temperature in air. Sodium borohydride ($NaBH_4$, 100 mM, 100 μL) is rapidly injected into this mixture to get the nanoplates.

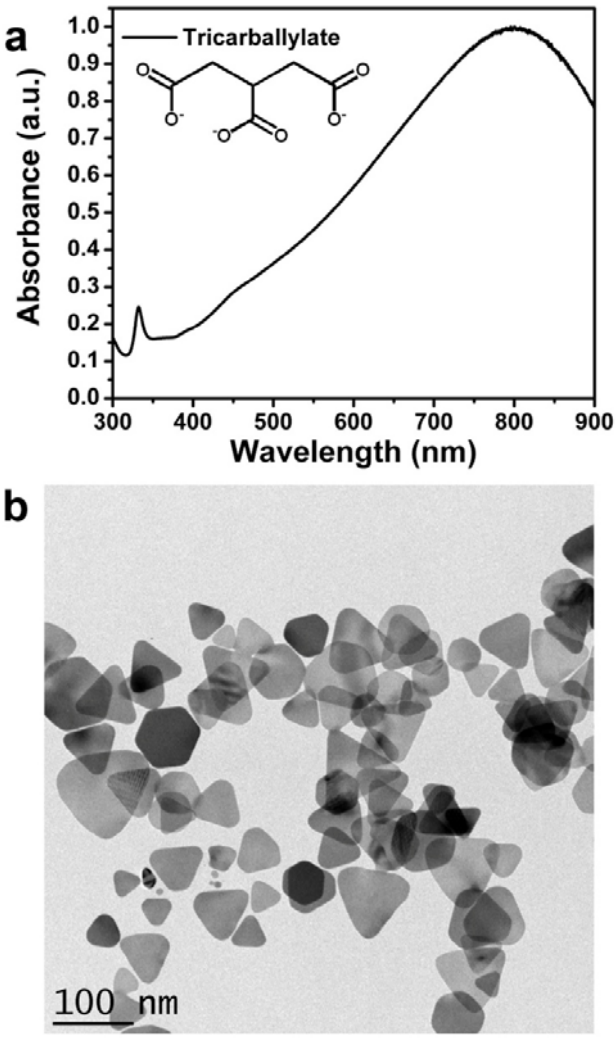


Figure S13 The UV-vis spectrum (a) and TEM image (b) of a typical sample prepared by substituting trisodium tricarballylate for trisodium citrate.

*Synthesis of silver nanoplates by using **tricarballylate*** Typically, the total volume of the reaction solution is fixed at 25.00 mL. In 24.14 mL of pure water, an aqueous solution of silver nitrate (0.05 M, 50 μL), trisodium tricarballylate (75 mM, 0.5 mL), poly (vinylpyrrolidone) (PVP, weight-average molecular weight Mw ~ 29, 000 g/mol, 17.5 mM, 0.1 mL), and hydrogen peroxide (30 wt. %, 60 μL) were combined and vigorously stirred at room temperature in air. Sodium borohydride ($NaBH_4$, 100 mM, 150 μL) is rapidly injected into this mixture to get the nanoplates.

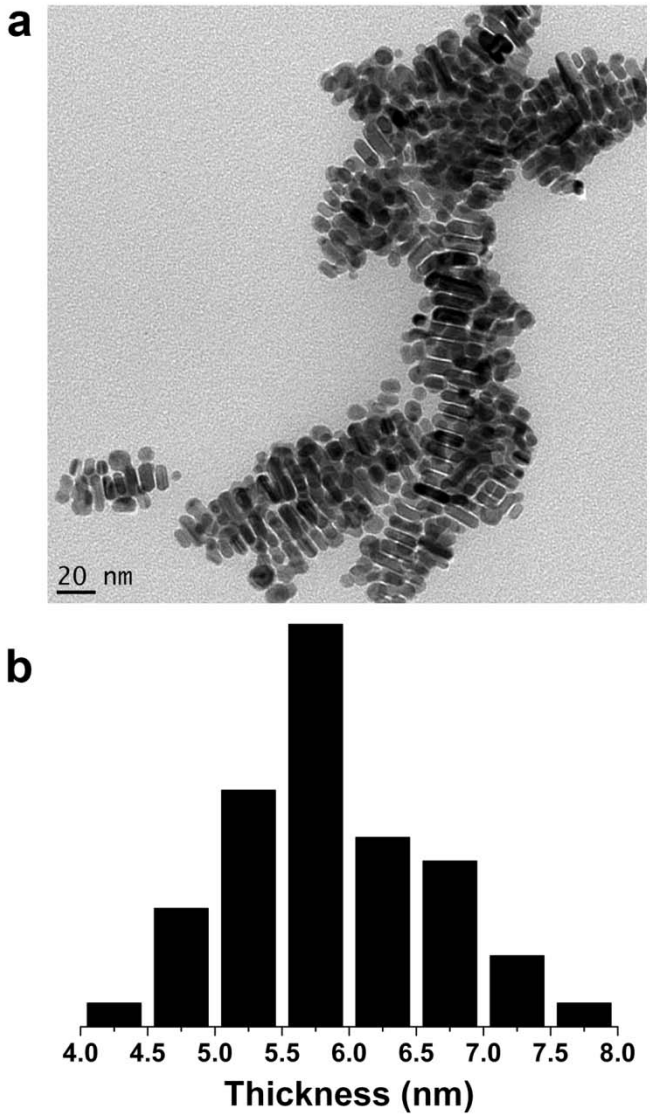


Figure S14 TEM image (a) and the histogram (b) of thickness when the concentration of $NaBH_4$ is 0.4 mM while the other conditions keep the same.

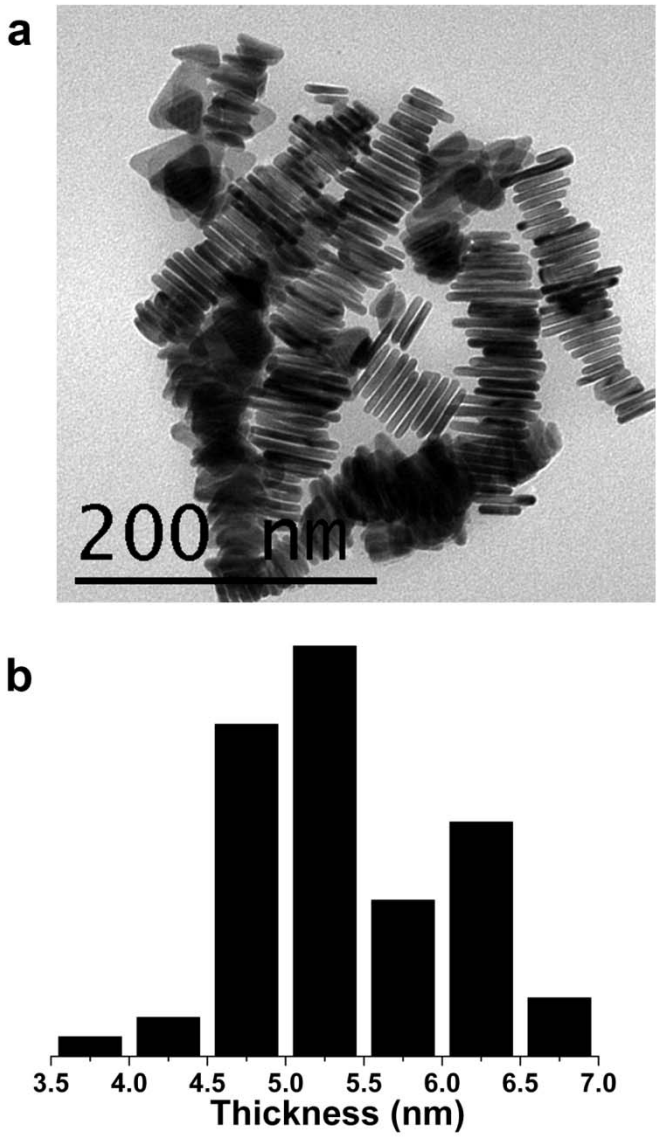


Figure S15 TEM image (a) and the histogram (b) of thickness when the concentration of $NaBH_4$ is 0.6 mM while the other conditions keep the same.

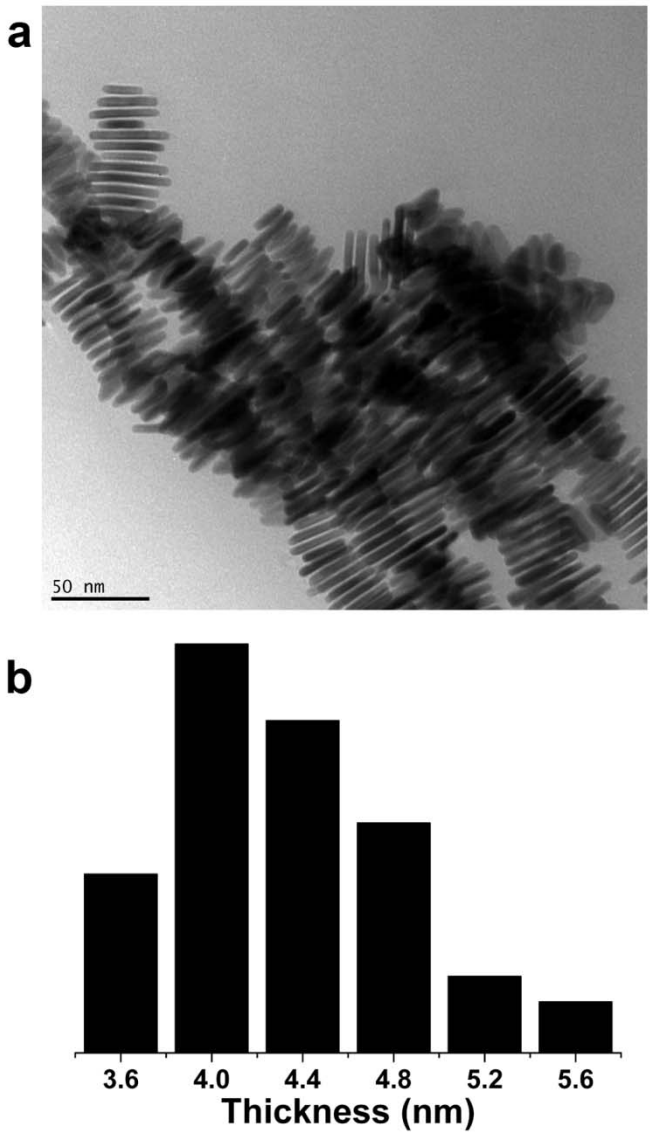


Figure S16 TEM image (a) and the histogram (b) of thickness when the concentration of $NaBH_4$ is 0.8 mM while the other conditions keep the same.

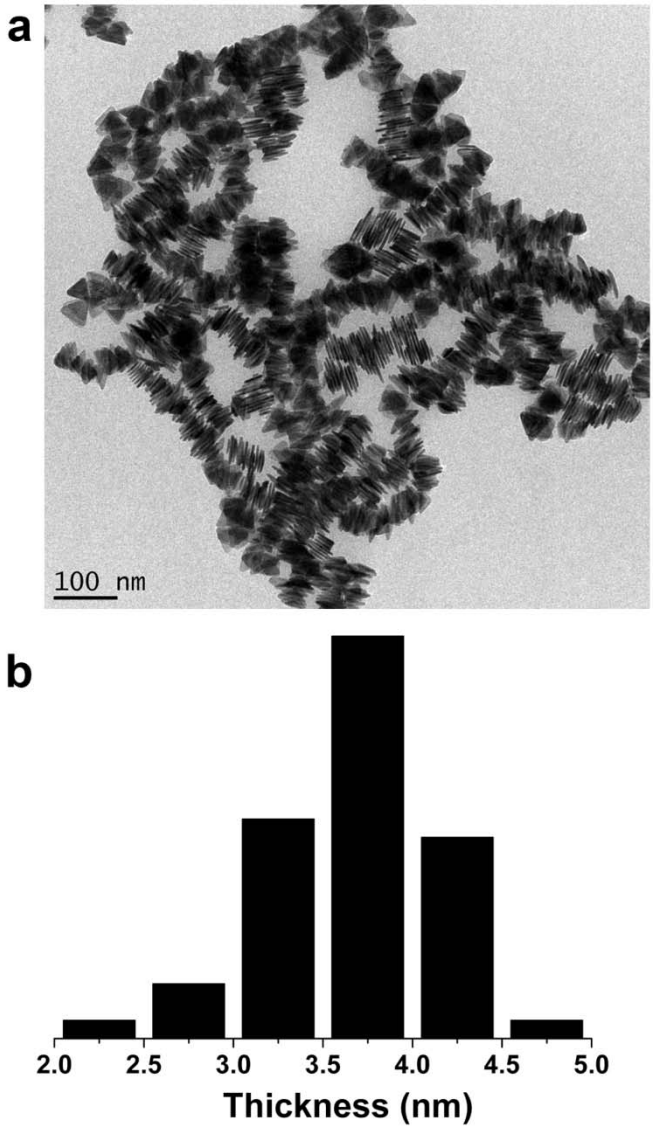


Figure S17 TEM image (a) and the histogram (b) of thickness when the concentration of $NaBH_4$ is 1.0 mM while the other conditions keep the same.

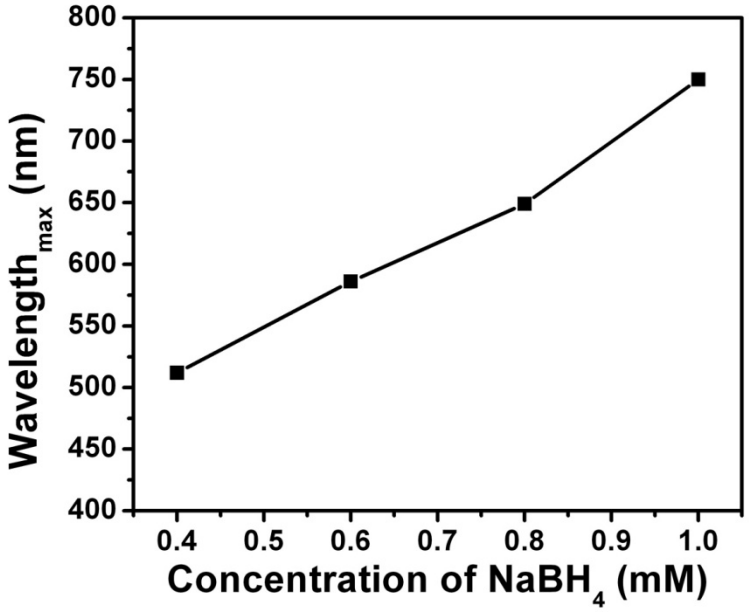


Figure S18 The position of the surface plasmon band as a function of the concentration of $NaBH_4$.

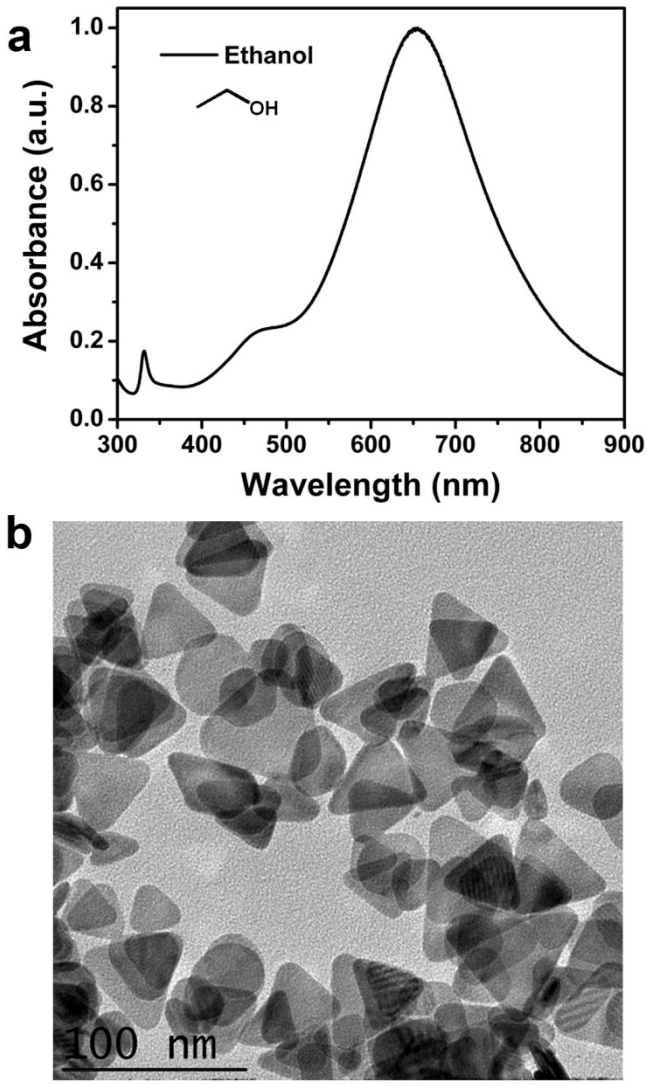


Figure S19 The UV-vis spectrum (a) and TEM image (b) of a typical sample prepared by substituting ethanol for PVP.

Synthesis of silver nanoplates by using ***ethanol*** Typically, the total volume of the reaction solution is fixed at 25.00 mL. In 24.14 mL of pure water, an aqueous solution of silver nitrate (0.05 M, 50 μL), trisodium citrate (75 mM, 0.5 mL), ethanol (17.5 mM, 0.1 mL), and hydrogen peroxide (30 wt. %, 60 μL) were combined and vigorously stirred at room temperature in air. Sodium borohydride ($NaBH_4$, 100 mM, 150 μL) is rapidly injected into this mixture to get the nanoplates.

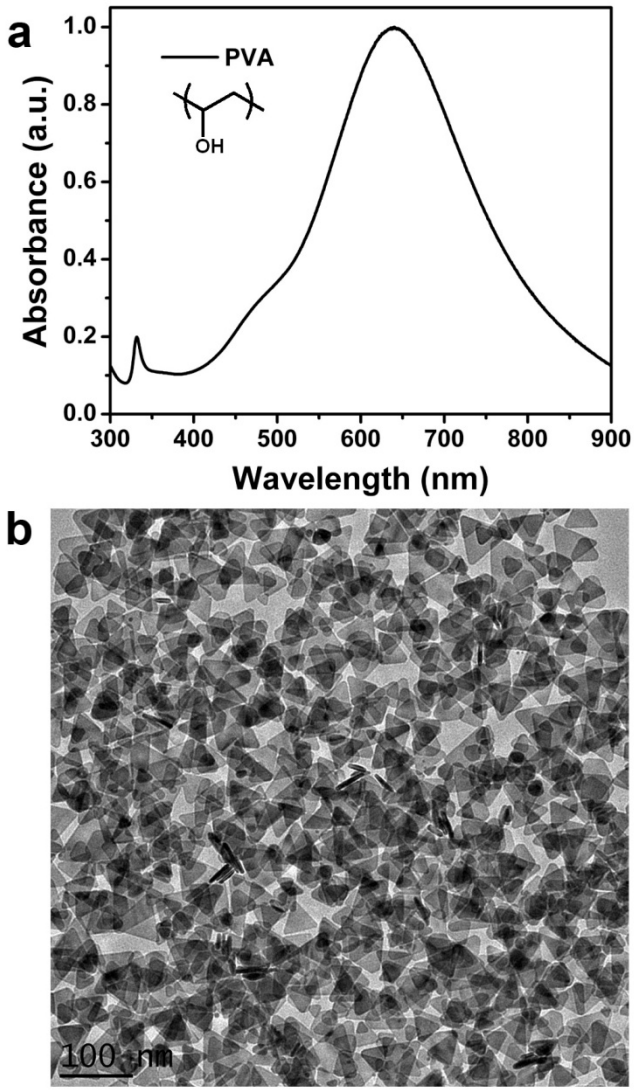


Figure S20 The UV-vis spectrum (a) and TEM image (b) of a typical sample prepared by substituting polyvinyl alcohol (PVA) (Mw ~ 88,000) for PVP.

*Synthesis of silver nanoplates by using **PVA*** Typically, the total volume of the reaction solution is fixed at 25.00 mL. In 24.14 mL of pure water, an aqueous solution of silver nitrate (0.05 M, 50 μL), trisodium citrate (75 mM, 0.5 mL), polyvinyl alcohol (PVA, Mw ~ 88,000, 17.5 mM, 0.1 mL), and hydrogen peroxide (30 wt. %, 60 μL) were combined and vigorously stirred at room temperature in air. Sodium borohydride ($NaBH_4$, 100 mM, 150 μL) is rapidly injected into this mixture to get the nanoplates.

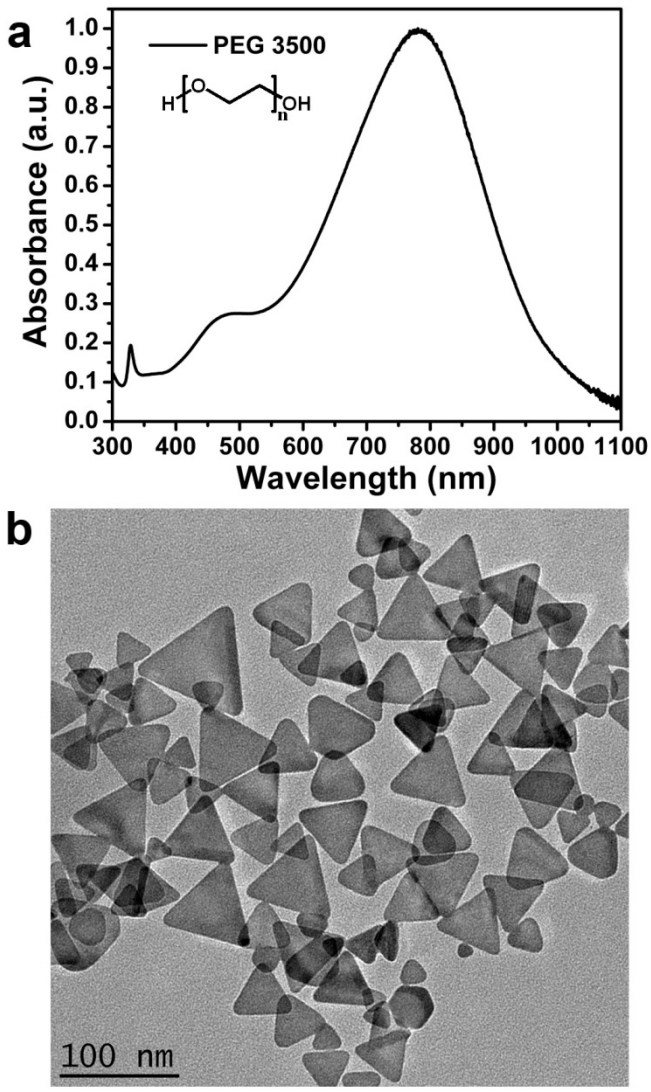


Figure S 21 The UV-vis spectrum (a) and TEM image (b) of a typical sample prepared by substituting polyethylene glycol (PEG) (Mw ~ 3,500) for PVP.

*Synthesis of silver nanoplates by using **PEG*** Typically, the total volume of the reaction solution is fixed at 25.00 mL. In 24.14 mL of pure water, an aqueous solution of silver nitrate (0.05 M, 50 μL), trisodium citrate (75 mM, 0.5 mL), polyethylene glycol (PEG, Mw ~ 3,500, 17.5 mM, 0.1 mL), and hydrogen peroxide (30 wt. %, 60 μL) were combined and vigorously stirred at room temperature in air. Sodium borohydride ($NaBH_4$, 100 mM, 150 μL) is rapidly injected into this mixture to get the nanoplates.

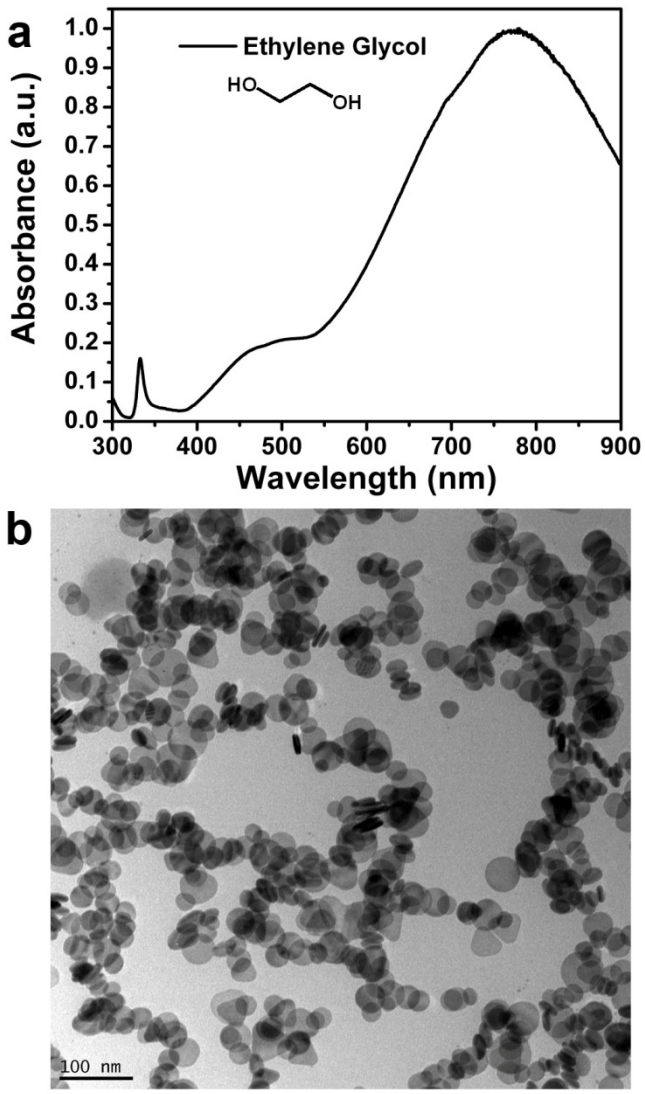


Figure S22 The UV-vis spectrum (a) and TEM image (b) of a typical sample prepared by substituting ethylene glycol (EG) for PVP.

Synthesis of silver nanoplates by using ***ethylene glycol*** Typically, the total volume of the reaction solution is fixed at 25.00 mL. In 24.04 mL of pure water, an aqueous solution of silver nitrate (0.05 M, 50 μL), trisodium citrate (75 mM, 0.5 mL), ethylene glycol (EG, 17.5 mM, 0.1 mL), and hydrogen peroxide (30 wt. %, 60 μL) were combined and vigorously stirred at room temperature in air. Sodium borohydride ($NaBH_4$, 100 mM, 250 μL) is rapidly injected into this mixture to get the nanoplates.

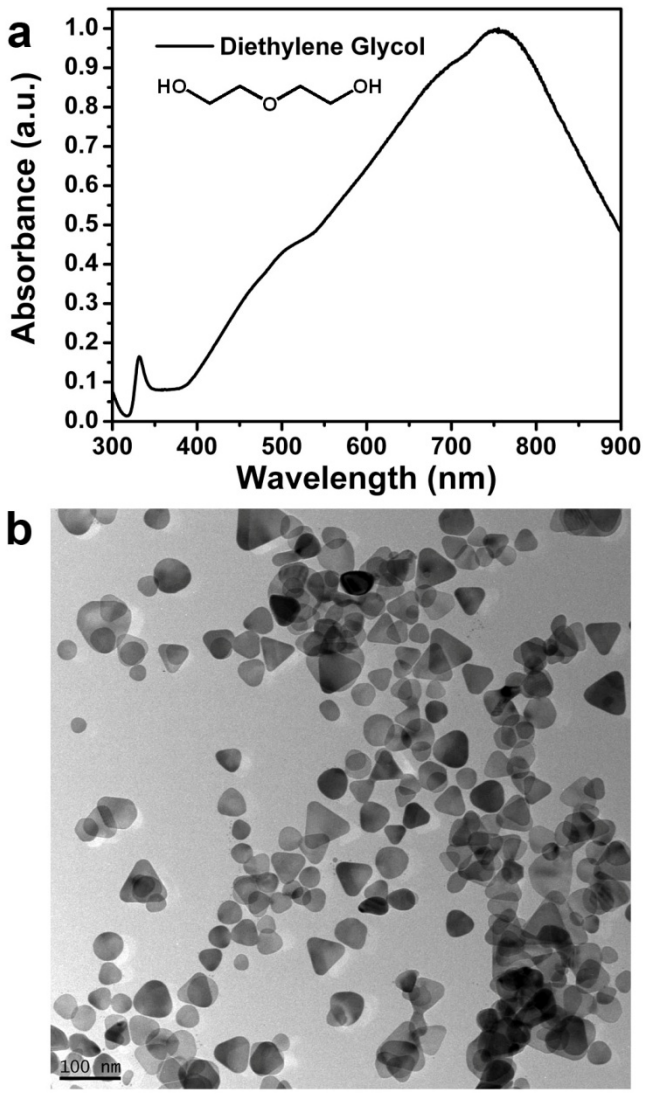


Figure S23 The UV-vis spectrum (a) and TEM image (b) of a typical sample prepared by substituting diethylene glycol (DEG) for PVP.

Synthesis of silver nanoplates by using ***diethylene glycol*** Typically, the total volume of the reaction solution is fixed at 25.00 mL. In 24.04 mL of pure water, an aqueous solution of silver nitrate (0.05 M, 50 μL), trisodium citrate (75 mM, 0.5 mL), diethylene glycol (DEG, 17.5 mM, 0.1 mL), and hydrogen peroxide (30 wt. %, 60 μL) were combined and vigorously stirred at room temperature in air. Sodium borohydride ($NaBH_4$, 100 mM, 250 μL) is rapidly injected into this mixture to get the nanoplates.

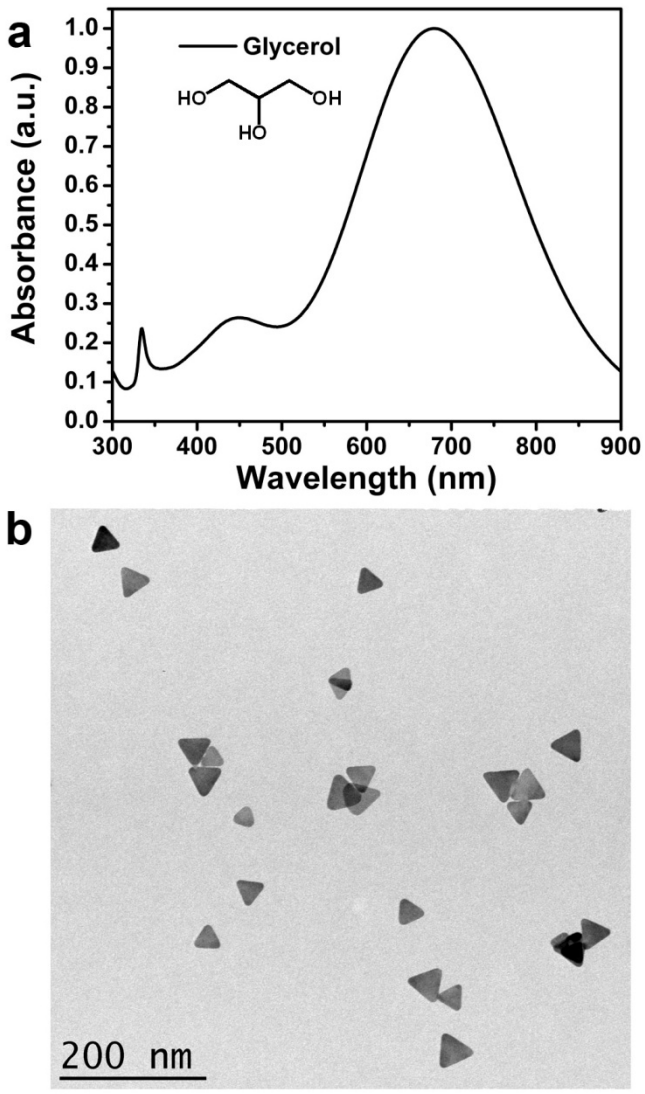


Figure S24 The UV-vis spectrum (a) and TEM image (b) of a typical sample prepared by substituting glycerol for PVP.

*Synthesis of silver nanoplates by using **glycerol*** Typically, the total volume of the reaction solution is fixed at 25.00 mL. In 24.04 mL of pure water, an aqueous solution of silver nitrate (0.05 M, 50 μL), trisodium citrate (75 mM, 0.5 mL), glycerol (17.5 mM, 0.1 mL), and hydrogen peroxide (30 wt. %, 60 μL) were combined and vigorously stirred at room temperature in air. Sodium borohydride ($NaBH_4$, 100 mM, 250 μL) is rapidly injected into this mixture to get the nanoplates.

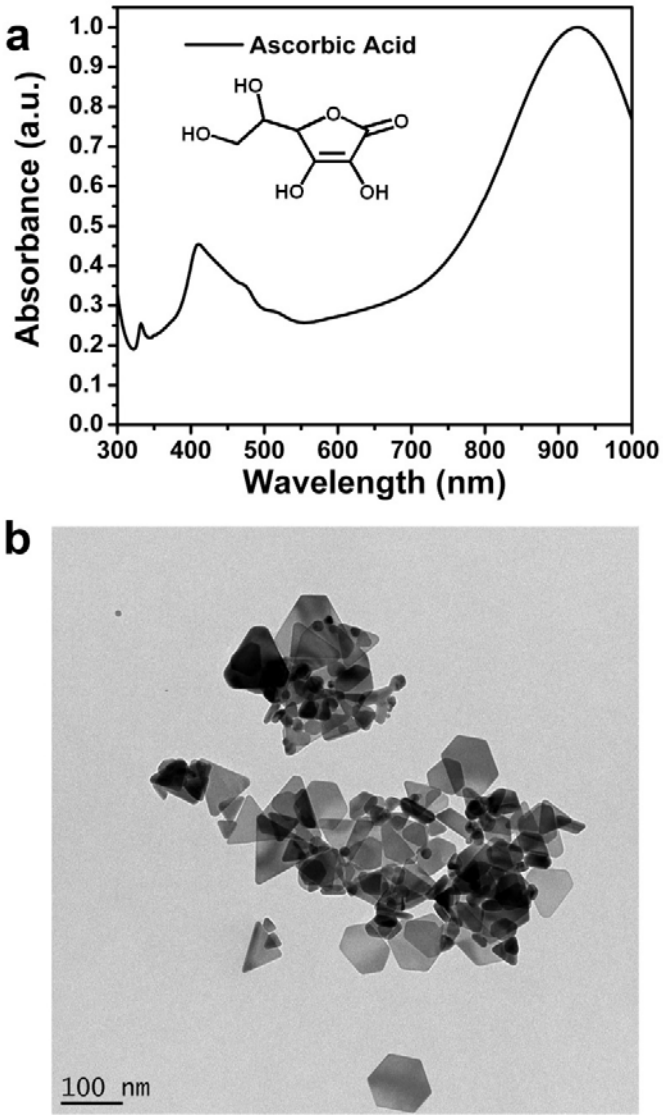


Figure S25 The UV-vis spectrum (a) and TEM image (b) of a typical sample prepared by substituting ascorbic acid for $NaBH_4$.

*Synthesis of silver nanoplates by using **ascorbic acid*** Typically, the total volume of the reaction solution is fixed at 25.00 mL. In 24.04 mL of pure water, an aqueous solution of silver nitrate (0.05 M, 50 μL), trisodium citrate (75 mM, 0.5 mL), poly (vinylpyrrolidone) (PVP, weight-average molecular weight Mw ~ 29, 000 g/mol, 17.5 mM, 0.1 mL), and hydrogen peroxide (30 wt. %, 60 μL) were combined and vigorously stirred at room temperature in air. Sodium ascorbate (100 mM, 250 μL) is rapidly injected into this mixture to get the nanoplates.

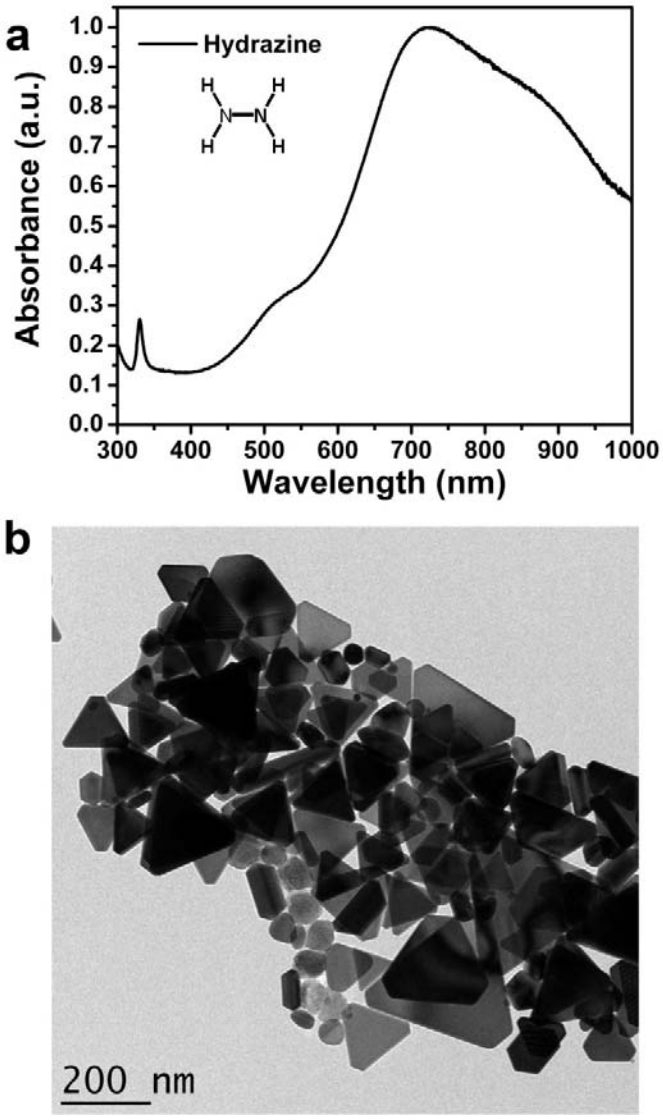


Figure S26 The UV-vis spectrum (a) and TEM image (b) of a typical sample prepared by substituting hydrazine for $NaBH_4$.

Synthesis of silver nanoplates by using ***hydrazine*** Typically, the total volume of the reaction solution is fixed at 25.00 mL. In 24.19 mL of pure water, an aqueous solution of silver nitrate (0.05 M, 50 μL), trisodium citrate (75 mM, 0.5 mL), poly (vinylpyrrolidone) (PVP, weight-average molecular weight Mw ~ 29, 000 g/mol, 17.5 mM, 0.1 mL), and hydrogen peroxide (30 wt. %, 60 μL) were combined and vigorously stirred at room temperature in air. Hydrazine hydrate (hydrazine 64%, 100 μL) is rapidly injected into this mixture to get the nanoplates.