

Supporting Information

Metal Ion Redox Potential Plays an Important Role in High-Yield Synthesis of Monodisperse Silver Nanoparticles

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Table S1. Statistical results of average diameter for the samples A-F in Figure S1.

	Average diameter (nm)	Standard deviation (SD)
A	3.9±0.1	2.56%
B	3.9±0.1	2.56%
C	4.0±0.15	3.75%
D	6±5.2	86.67%
E	8±4.7	58.75%
F	4.5±2.1	46.33%

300 particles were measured to get the size distribution.

Table S2. The corresponding results of AgNPs obtained with Fe^{3+} (A*) and without Fe^{3+} (B*) catalyzing in UV-Vis measurements of Figure 2B.

		120 °C	160 °C	200 °C
A*: OA+OAM+ Fe^{3+}	I_{peak}	0.66933	0.99951	1.06879
	λ_{max}	412 nm	412 nm	412 nm
	FWHM	85 nm	78 nm	75 nm
B*: OA+OAM	I_{peak}	0.09210	0.59324	0.87793
	λ_{max}	419 nm	421 nm	414 nm
	FWHM	105 nm	103 nm	86 nm

The volumes of OA and OAM used in the reaction were both 10 mL. The amount of Fe^{3+} added was 0.1 mmol. FWHM = full width at half maximum. I_{peak} was the intensity of the absorption peak.

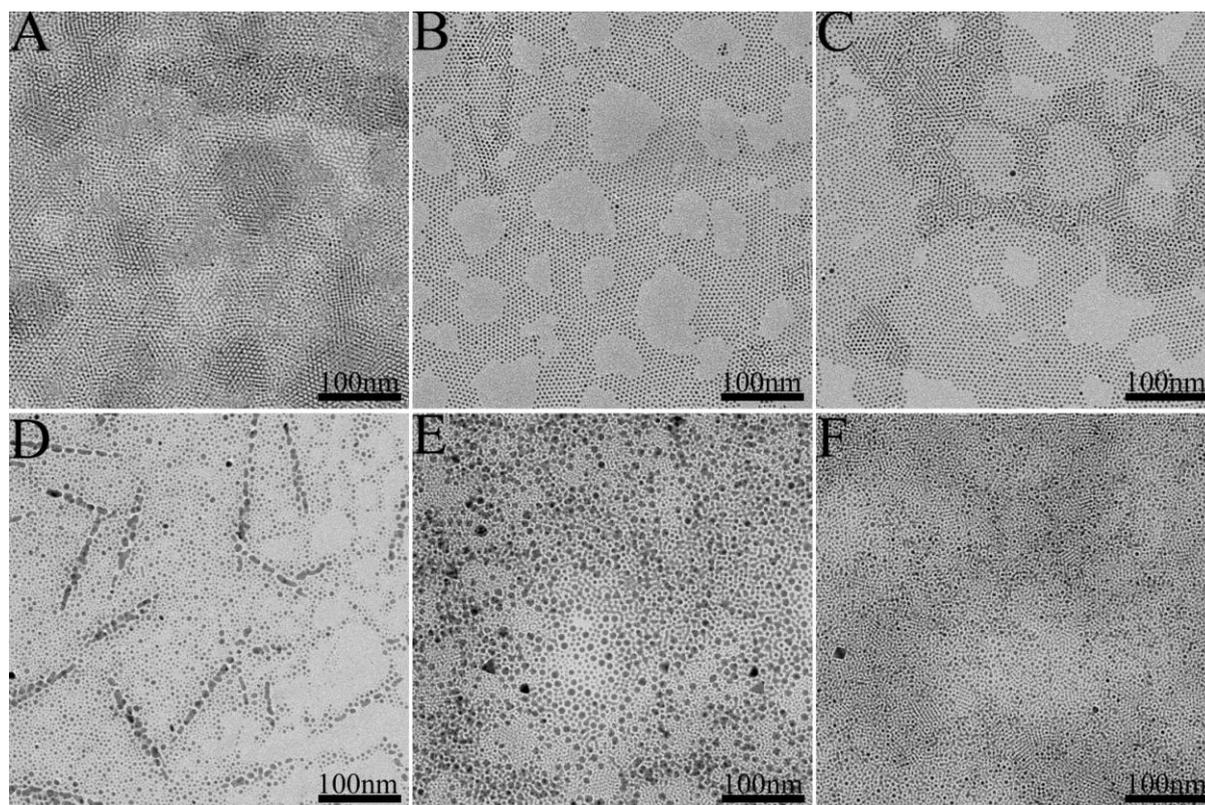


Figure S1. TEM images of AgNPs obtained with or without adding Fe³⁺ ions at different reaction temperatures. A-C: 120 °C, 160 °C, and 200 °C with adding Fe³⁺ ions; D-F: 120 °C, 160 °C, 200 °C without adding Fe³⁺ ions, respectively. The volumes of OA and OAM used in the reaction were both 10 mL.

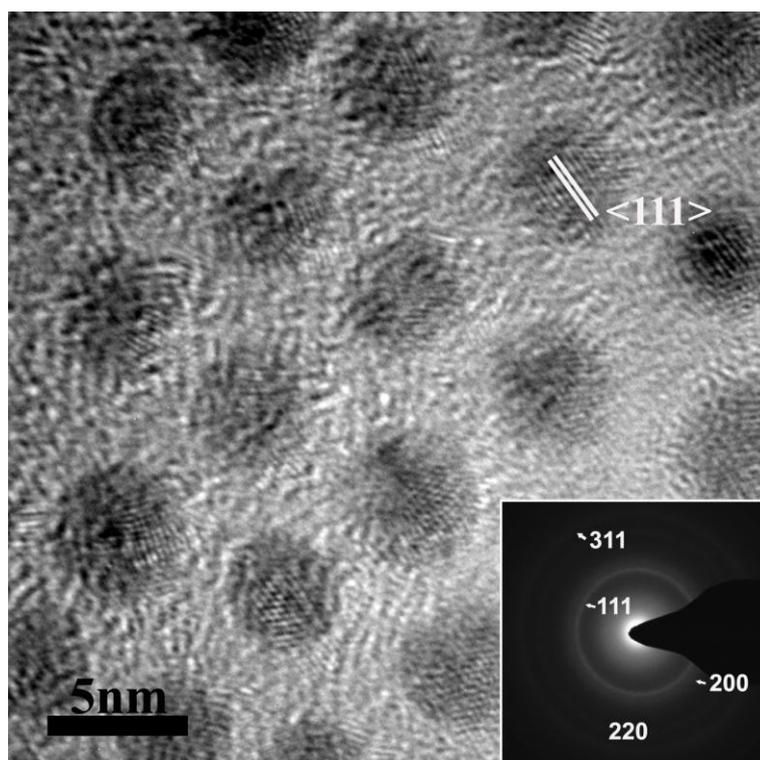


Figure S2. HR-TEM image of the as-prepared AgNPs with addition of Fe^{3+} in the reaction at $120\text{ }^\circ\text{C}$. It was found that most of the AgNPs were polycrystalline. Inset showed selected area electron diffraction (SAED) patterns of the as-prepared 4-nm sized AgNPs.

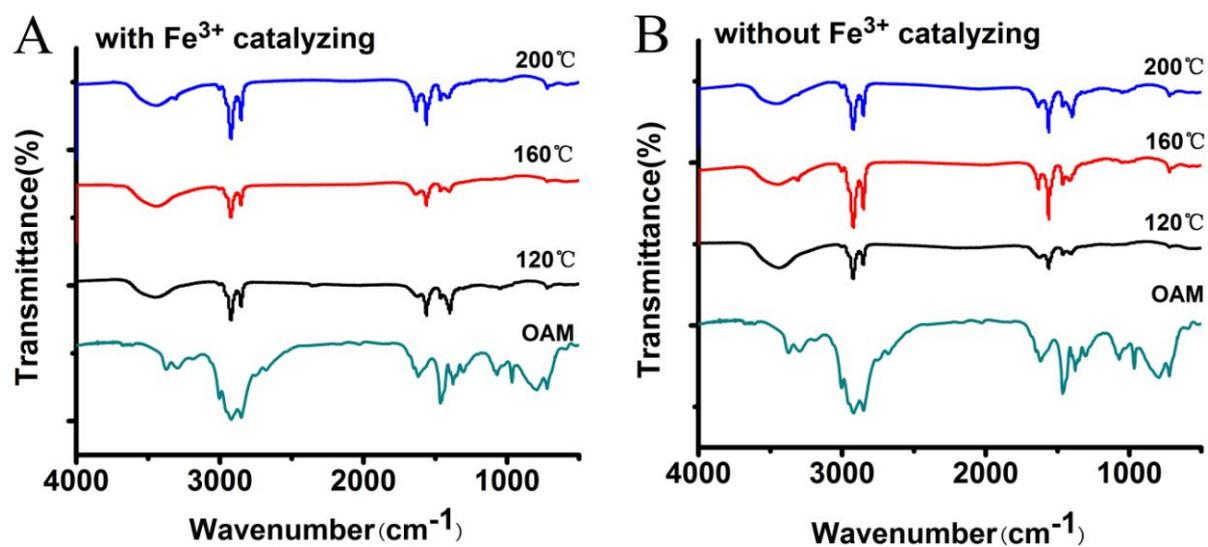


Figure S3. Fourier transform infrared spectrometer (FTIR) spectra of the AgNPs. A: with adding Fe³⁺; B: without adding Fe³⁺. The volumes of OA and OAM used in the reaction were both 10 mL for all samples.

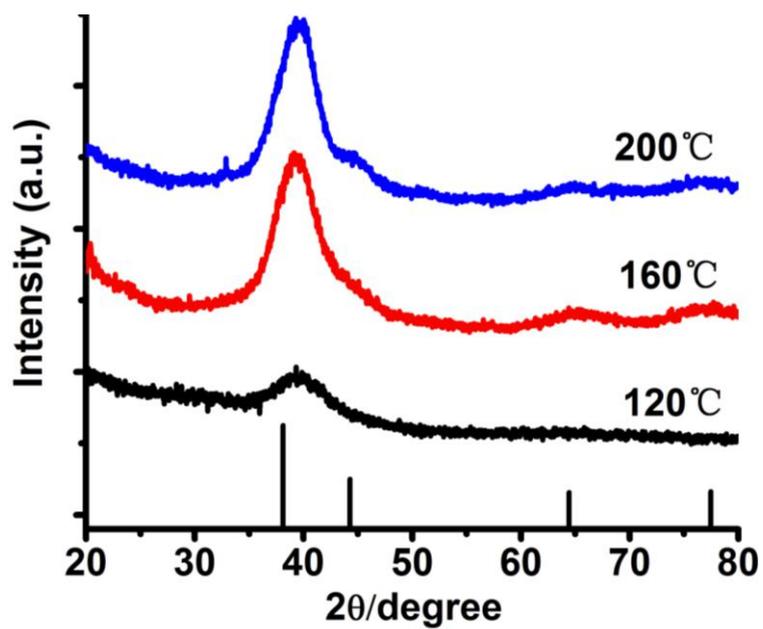


Figure S4. XRD patterns of the AgNPs without adding Fe^{3+} at three different reaction temperatures under N_2 atmosphere. The volume of OA and OAM used in the reaction were both 10 mL for all samples.

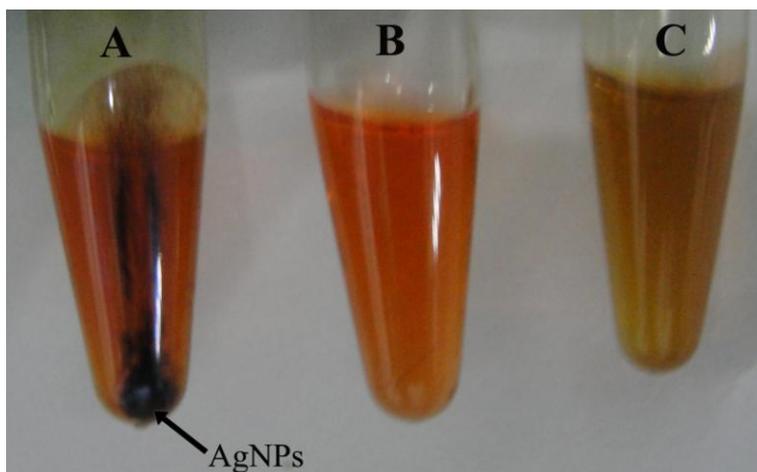


Figure S5. Determination of Fe^{2+} ions in the reaction employing the standard 1,10-phenanthroline spectrophotometry method. Once there are Fe^{2+} ions in the solution, the intrinsic orange-red color of the Fe^{2+} -1,10-phenanthroline complex will be observed by adding 1,10-phenanthroline into the solution. A: Optical picture of the 1,10-phenanthroline coordinated supernatant of the reaction system at the end of AgNPs synthesis with adding Fe^{3+} at 120 °C. 100 μL of the resulted mixture were extracted by centrifuging at 13000 rpm for 5 min with adding 200 μL of acetic acid-sodium acetate buffer solution ($\text{pH} \approx 4.5$) and 200 μL of ethanol containing 1,10-phenanthroline (0.2 %). The intrinsic orange-red color of Fe^{2+} -1,10-phenanthroline was observed, indicating the existence of Fe^{2+} . Two control experiments were designed to confirm the conclusion. B: Only Fe^{3+} were added into the mixture of OA-OAM without addition of AgNO_3 while keeping other parameters same, orange-red color was observed. C: only AgNO_3 was added into the mixture of OA-OAM without addition of Fe^{3+} while keeping other parameters same, no orange-red color was observed.

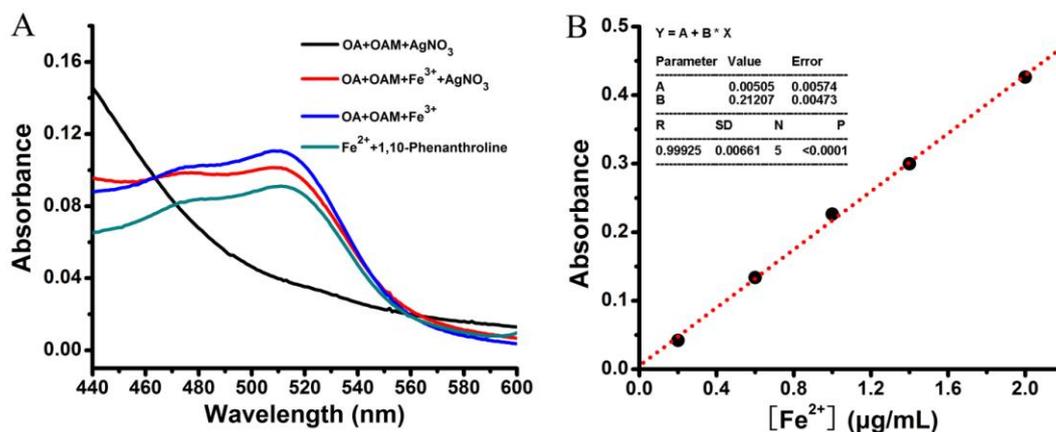


Figure S6. Determination of the concentration of Fe^{2+} by 1,10-phenanthroline using UV-Vis spectrometry. A: UV-Vis spectra of the Fe^{2+} -1,10-phenanthroline complexes of different reactions. The characteristic absorption feature of Fe^{2+} -1,10-phenanthroline was presented in the region of 500-520 nm; B: Calibration curve of the concentration of Fe^{2+} ions was determined by choosing the absorbance peak intensity at $\lambda=510\text{nm}$.

According to Figure S6A, the peak intensity at $\lambda=510\text{nm}$ for system with adding AgNO_3 ($I_1, \lambda_{510\text{nm}}$) and without adding AgNO_3 ($I_2, \lambda_{510\text{nm}}$) in the presence of Fe^{2+} were 0.10129 and 0.11048, respectively. So, the resulted concentration of Fe^{2+} for the reaction system with adding AgNO_3 (c_1) and without adding AgNO_3 (c_2) were calculated as following:

$$c_1 = \frac{(0.10129 - 0.00505)}{0.21207} \times 12.5 = 5.6727 \mu\text{g/mL};$$

$$c_2 = \frac{(0.11048 - 0.00505)}{0.21207} \times 12.5 = 6.2143 \mu\text{g/mL};$$

The value 12.5 presented volume dilution times for the initial $[\text{Fe}^{2+}]$. The conversion efficiency of $\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$ for the system with adding AgNO_3 (w_1) and without AgNO_3 (w_2) in the presence of Fe^{2+} were:

$$w_1 = \frac{5.6727 \times 10^{-6} \text{g/mL} \times 20 \text{mL}}{55.8457 \text{g/mol} \times \left(\frac{0.04 \text{g}}{404 \text{g/mol}} \right)} \times 100\% = 2.03\%$$

$$w_2 = \frac{6.2143 \times 10^{-6} \text{g/mL} \times 20 \text{mL}}{55.8457 \text{g/mol} \times \left(\frac{0.04 \text{g}}{404 \text{g/mol}} \right)} \times 100\% = 2.23\%$$

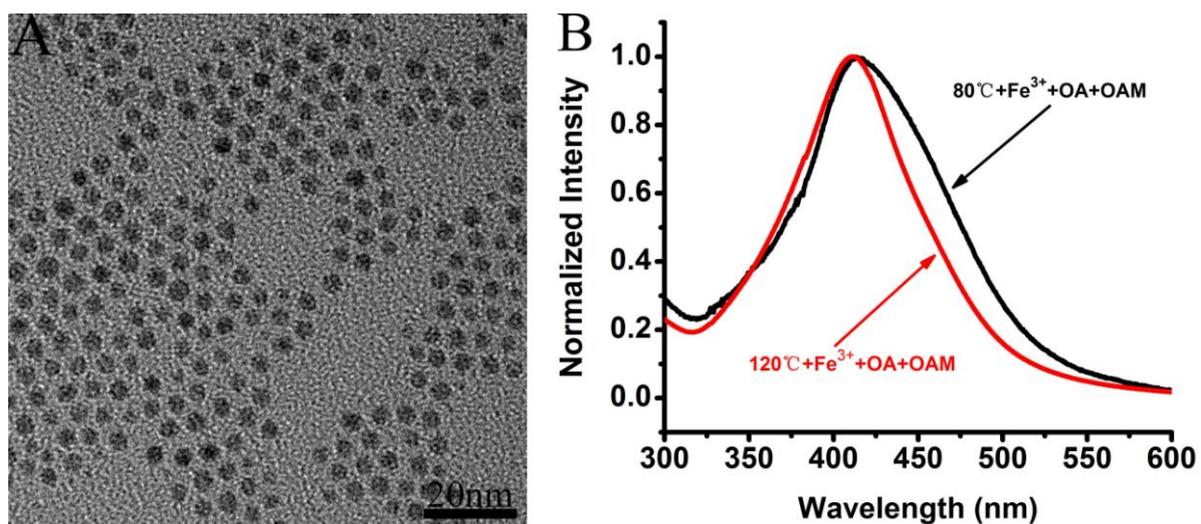


Figure S7. TEM image (A) and UV-Vis spectra (B) of the AgNPs at 80 °C with adding Fe³⁺ ions. The size distribution was calculated by measuring 300 particles to be 4.0 ± 0.1 nm in diameter. The peak position in UV-Vis spectrum is $\lambda_{\text{max}} = 413$ nm with FWHM ~ 95 nm. The volumes of OA and OAM used in the reaction were both 10 mL for all samples at N₂ atmosphere.

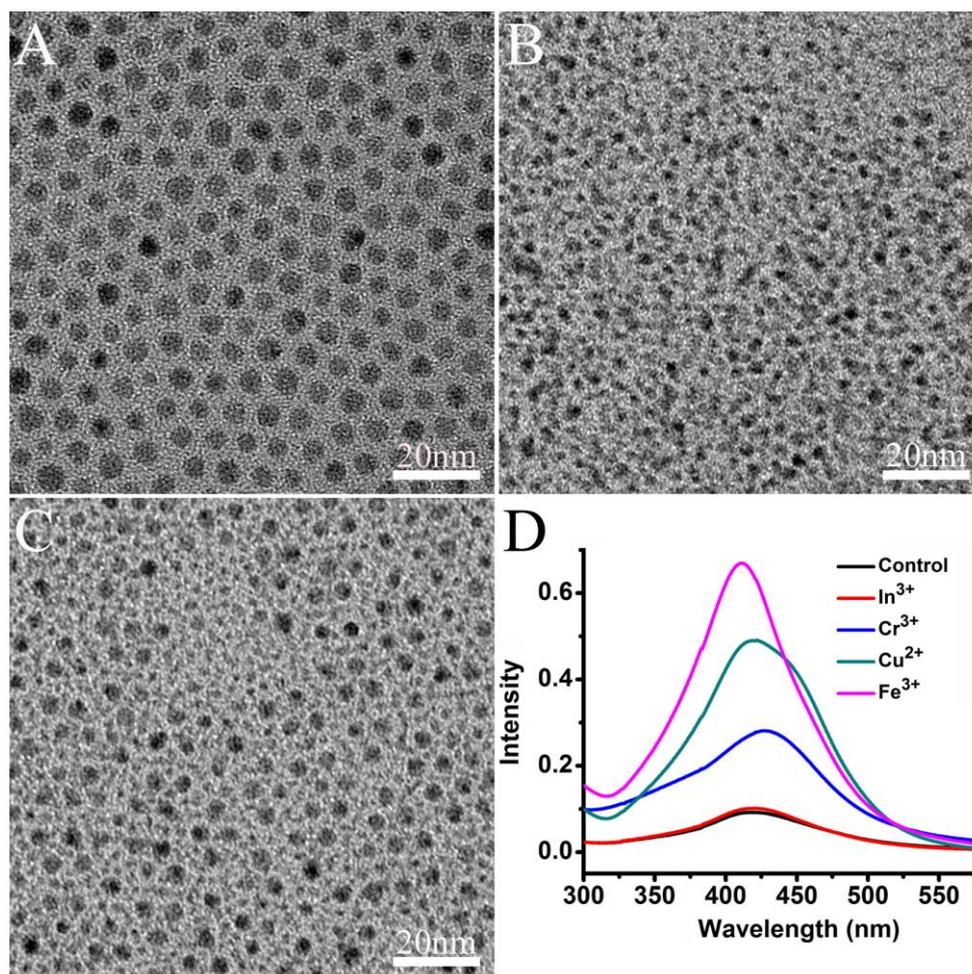


Figure S8. TEM images (A-C) and UV-vis spectra (D) of the AgNPs catalyzed with different metal ions at 120 °C. A: Cu^{2+} ions; B: Cr^{3+} ions; C: In^{3+} ions. As shown in Figure S5A, the reaction with addition of Cu^{2+} ions produced monodispersed AgNPs with the diameter of 6 nm and size distribution of 9 %, whereas the reactions added with Cr^{3+} and In^{3+} ions did not provide uniform AgNPs but some smaller NPs in wide size distributions (Figures S5B and S5C, Table S3). The UV-Vis spectra in Figure S5D presented the relative yield of AgNPs and their sizes and size distributions from the reactions with addition of Cu^{2+} , Cr^{3+} and In^{3+} ions under the same conditions, respectively. It was observed that the Cu^{2+} ions significantly improved the yield of AgNPs in comparison with the reaction without adding any metal ions, although the yield was a little lower than that of the reaction with addition of Fe^{3+} ions. For the reaction with adding Cr^{3+} ions, a weakened catalytic effect on the production of AgNPs was observed, while the addition of In^{3+} ions did not improve the yield of AgNPs. In the meantime, the FWHMs of the UV-Vis spectra depicted that the quality of the AgNPs from the reaction catalyzed by Cu^{2+} ions was better than those of adding Cr^{3+} and In^{3+} in terms of the size distribution.

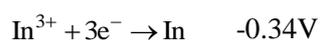
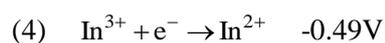
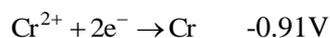
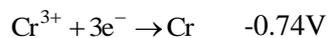
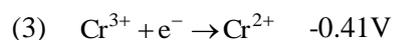
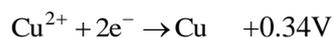
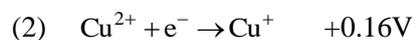
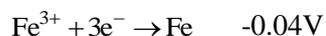
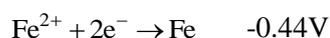
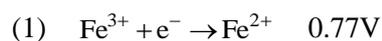
We reasoned that the redox potential of the metal ion played the vital role in determining the yield and quality of AgNPs. The redox potential of $\text{Cu}^{2+}/\text{Cu}^{+}$ is +0.16 V which is higher than that of $\text{Cr}^{3+}/\text{Cr}^{2+}$ (-0.41 V) and $\text{In}^{3+}/\text{In}^{2+}$ (-0.49 V), so in the case of adding Cu^{2+} ions in the reaction, the Cu^{2+} was reduced into Cu^{+} with accepting one electron from OAM and then the Cu^{+} donated one electron to Ag^{+} to form the Ag atom as the nucleation center of AgNPs. This circled self-catalyzing process helped to improve the yield of AgNPs. However, for the reactions with adding Cr^{3+} and In^{3+} ions, their redox potentials did not match with that of Ag^{+}/Ag and OAM, which resulted in the circled self-catalyzing process performed in a low efficiency and thus the decreased yield of AgNPs. With regard to the size distribution of the AgNPs, the self-catalyzing circle with proper catalysts, such as Fe^{3+} and Cu^{2+} ions, promoted the kinetics contribution on the formation of AgNPs at the lower reaction temperature (120 °C), which fastened the nucleation process and further resulted in the monodispersed products. In contrast, the reactions added with Cr^{3+} and In^{3+} ions which possessed weak catalytic effect, were thermodynamically dominated and required an elongated nucleation stage at the lower reaction temperature (120 °C). The overlapped nucleation stage and growth stage of AgNPs resulted in the wide size distribution of the final products.^[1-3]

Table S3. The corresponding results of AgNPs in Figure 3.

	λ_{\max}	I_{peak}	FWHM	Average diameter (nm)	SD
Cu^{2+}	422 nm	0.491	106 nm	6.0 ± 0.55	9.17 %
Cr^{3+}	427 nm	0.28097	130 nm	2.0 ~ 7.0	55.56 %
In^{3+}	418 nm	0.10125	101 nm	1.8 ~ 5.5	50.68 %

The volume of OA and OAM were both 10 mL. The amount of metal ions added were ~10mol % of $[\text{Ag}^+]$.

The redox potentials of corresponding metal ions are shown as following:



References:

- (1) J. Park, K. An, Y. Hwang, J.-G. Park, H.-J. Noh, J.-Y. Kim, P.J.-H. ark, N.-M. Hwang, T. Hyeon, *Nat. Mater.*, 2004, **3**, 891.
- (2) Y. Xia, Y. Xiong, B. Lim, S. E. Skrabalak, *Angew. Chem. Int. Ed.*, 2009, **48**, 60.
- (3) R. Zhang, A. Khalizov, L. Wang, M. Hu, W. Xu, *Chem. Rev.*, 2011, DOI: 10.1021/cr2001756.