- Electronic Supplementary Information -

Ag Nanoframes: Controllable Reducing of $AgCl_xBr_{1-x}$ Nanocubes

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Materials

All chemical reagents were used without further purification. NaCl was purchased from Xilong Scientific Co.ltd. KBr and polyvinylpyrrolidone (M_W = 58000) were purchased from Aladdin. Ethylene glycol was purchased from Shanghai No.4 Reagent & H.v Chemical Co., Ltd. $AgNO_3$ was purchased from Sigma-Aldrich. Sodium borohydride (99.9%) was purchased from Fluka. Methylene blue was purchased from Sinopharm Chemical Reagent limited corporation. Ethanol was purchased from Fisher. Sodium citrate was purchased from Aladdin. Deionized water (resistance > 18.2 M/cm) was used in all reactions. All other chemicals were purchased from Sigma Aldrich. Copper specimen grids (300 mesh) with formvar/carbon support film were purchased from Beijing Zhongjingkeyi Technology Co, Ltd.

Methods

Characterization. TEM images were collected from a HT7700 Transmission Electron Microscopy operated at 100 kV and a Talos L 120C model operated at 120 kV and high-resolution transmission electron microscopy (HRTEM, JEM-2100, accelerating voltage 200 kV). SEM images were collected from a Quanta 250 FEG Scanning Transmission Electron Microscopy operated at 15 kV. X-ray diffraction (XRD) patterns were acquired by the Bruker D8 Advanced diffractometric using a Ni filtered Cu Kα radiation under 0.154 nm k value, and operated at 40 kV and 40 Ma. The X-ray photoelectron spectroscopy was collected in an Omicron ESCA Probe with a monochromatic Al K α source at 1486.6 eV. UV-Vis spectra were collected on a Lambd 750 UV-Vis spectrophotometer.

Synthesis of $AgCl_{0.91}Br_{0.09}$ nanocubes. The synthesis of $AgCl_{0.91}Br_{0.09}$ NC is based on the literature.[1] Typically, under a nitrogen atmosphere, NaCl (0.0179 g), KBr (0.0052 g), and PVP (2.6364 g) were added into 12 mL ethylene glycol. The mixture was incubated at 60 ^oC until all the materials are dissolved. Then, $AgNO_3$ (0.34 M, 1 mL in ethylene glycol) was injected to the mixture solution. The injection rate is 1 mL/min operated by a spring pump (KDS-200, KD Scientific, Holliston, MA). Finally, the mixture solution was incubated at 60 ^oC for 2 h. The synthesized $AgCl_{0.91}Br_{0.09}$ nanocubes were purified by ethanol two times.

Synthesis of Ag nanoframes. The purified $AgCl_{0.91}Br_{0.09}$ nanocube (500 μL) was concentrated to 10 μL via centrifugation (11000 rcf, 5 min). Then, the concentrated nanocubes were dispersed into PVP solution (0.06 M, 4 mL). After adding $NaBH_4$ (0.2 M, 90 μL), the mixture solution was stirred at room temperature for 50 min. The solution quickly changed from white to yellow and finally to grey, indicating the formation of Ag nanoframes.

Synthesis of Ag nanoparticles. The Ag nanoparticle (d = 35 nm) was synthesized according to the previous methods.[2] The solution containing 45 mL deionized water and 10 mL Au seeds (d = 10 nm) was heated at 135 ^{o}C under stirring. When the solution is boiling, sodium citrate (1%, 250 μL) and $AgNO_3$ (10 mg/mL, 250 μL) were added sequentially. The mixture solution was heated for 30 min. Then, the same amount of sodium citrate and $AgNO_3$ were added in, which was further heated for 30 min. Such process was repeated for another 11 times.

Reduction of Methylene blue. The catalytic degradation of methylene blue is based on the literature.[3] Catalytic reaction was carried out in a quartz cuvette and monitored by dynamic UV-Vis absorption spectra. 0.5 mL of Ag nanoframe was dispersed into 2.5 mL of MB dye solution (25 ppm), followed by rapid injection of 0.2 mL of $NaBH_4$ solution (0.2 M). The gradual change of the solution color from blue to colorless was observed during the reaction, indicating the transformation of methylene blue MB to leuco methylene blue (LMB).

The same procedure was carried out when 0.442 mL Ag nanoparticles replaced Ag nanoframes.

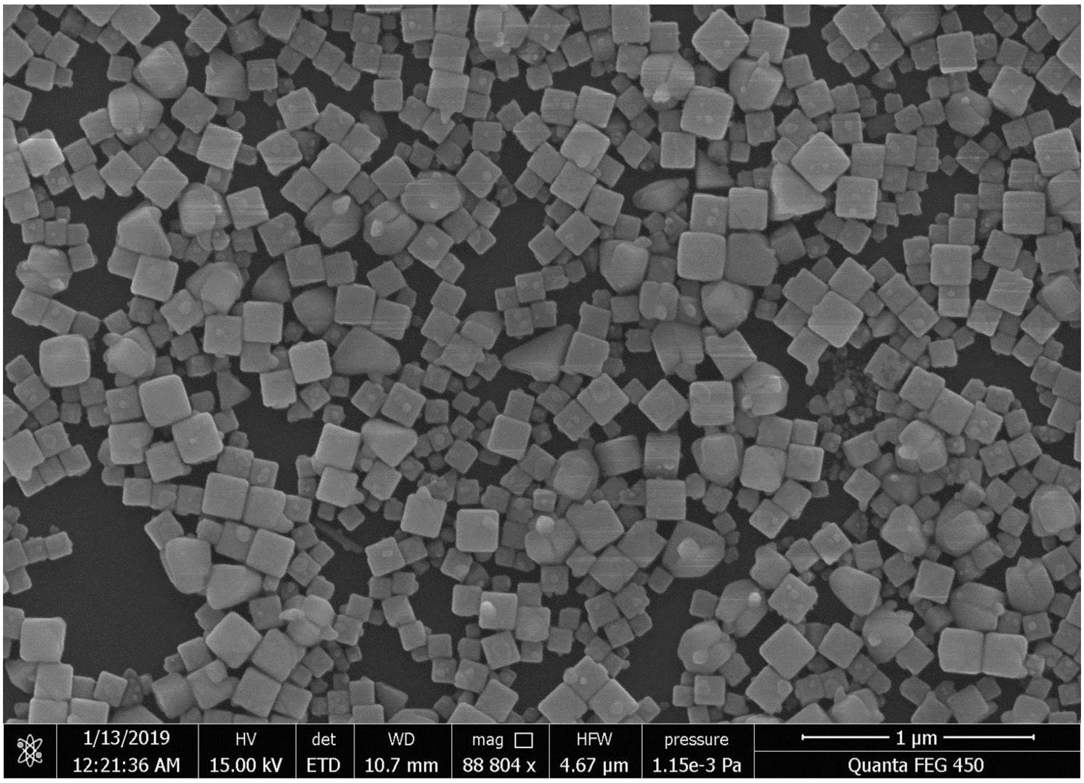

Figure S1 SEM image of $AgCl_{0.91}Br_{0.09}$ nanocubes.

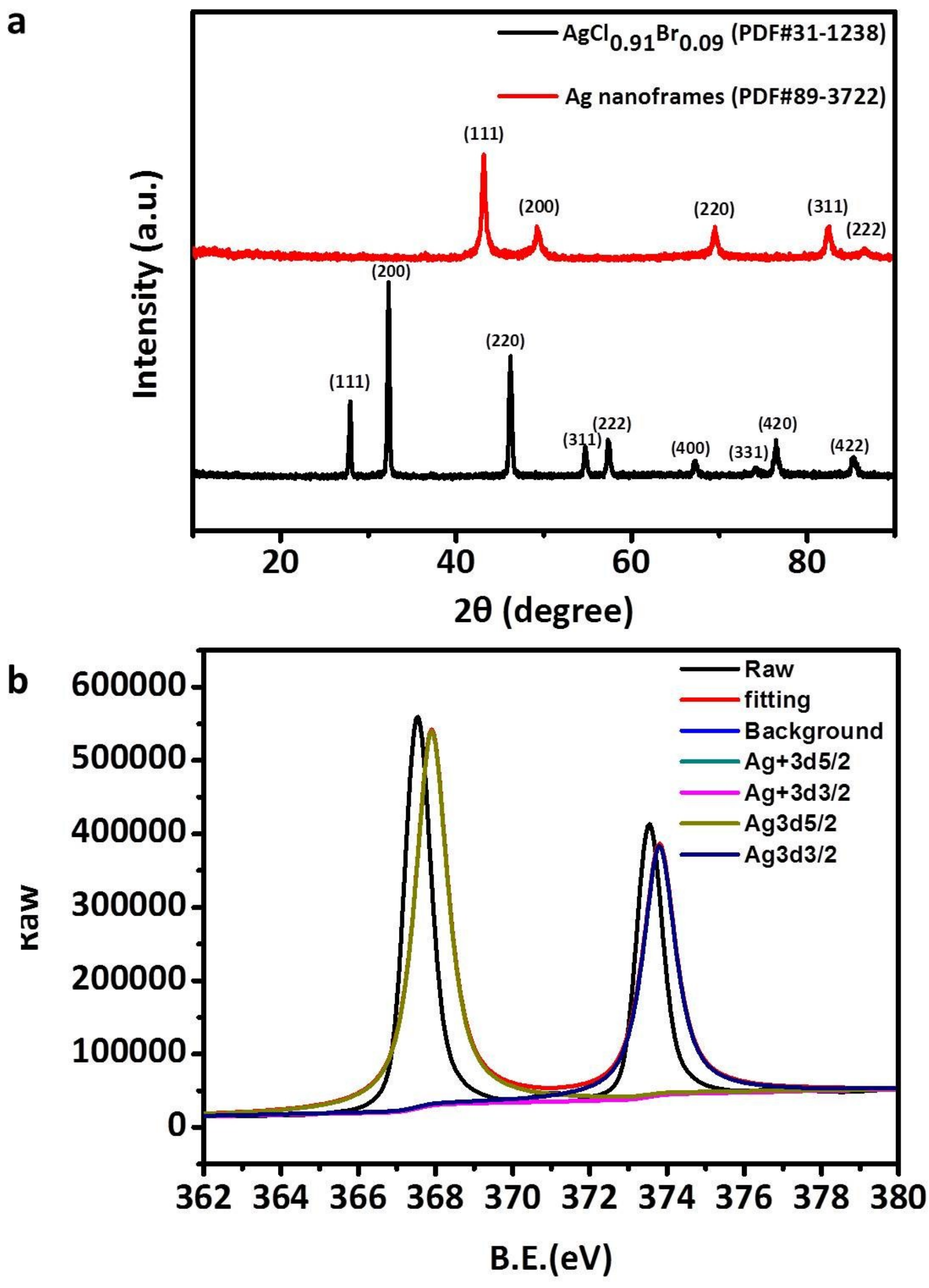

Figure S2 (a) XRD patterns of $AgCl_{0.91}Br_{0.09}$ nanocubes (black) and Ag nanoframes (red), respectively. (b) The XPS spectra of the Ag nanoframes: Ag 3d.

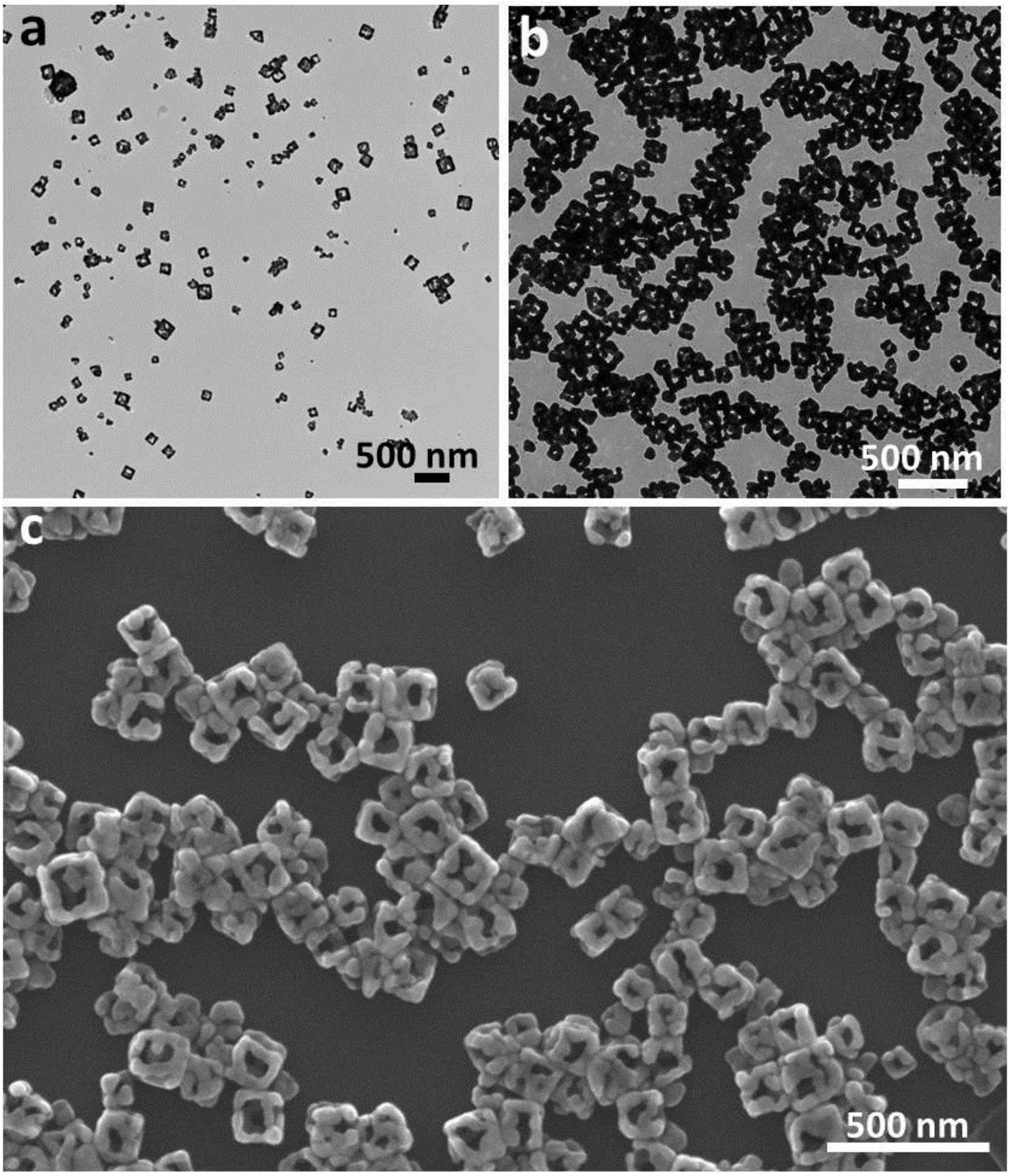

Figure S3 (a, b) TEM and (c) SEM images of Ag nanoframes.

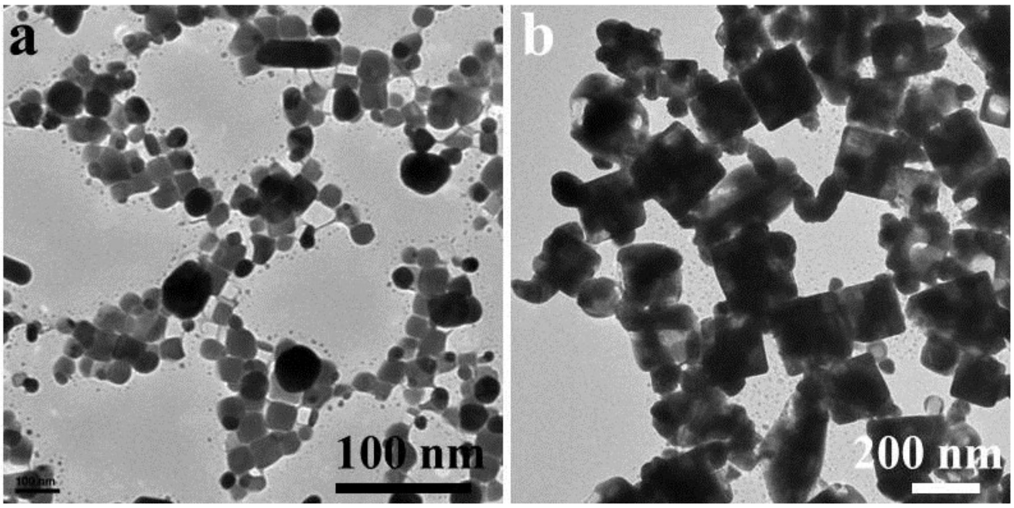

Figure S4 TEM images of the nanostructures synthesized with different reducing agents: (a) ascorbic acid, and (b) hydroquinone.

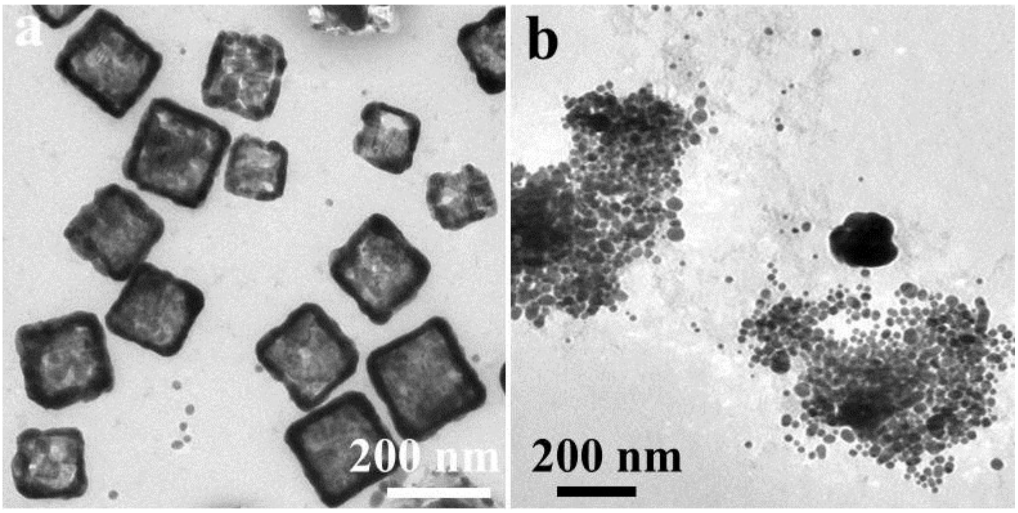

Figure S5 TEM images of the Ag hollow nanostructures synthesized at different temperature: (a) 0 ^{o}C, and (b) 60 ^{o}C.

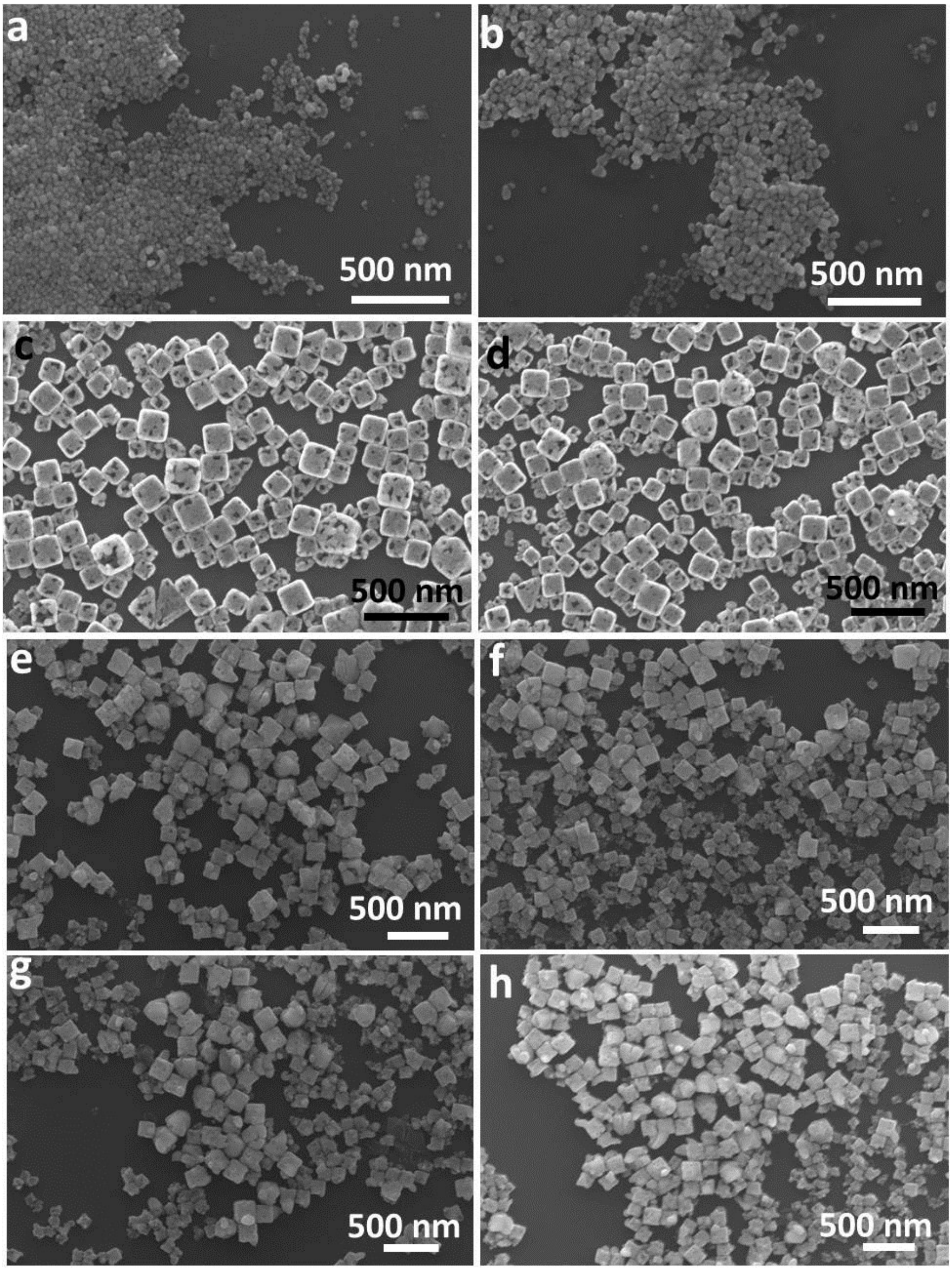

Figure S6 SEM images of the nanostructures synthesized with different concentration of $NaBH_4$: (a, b) 0.8 M, (c, d) 0.1 M, (e, f) 0.05 M, and (g, h) 6.2 $*10^{-3}$ M, respectively.

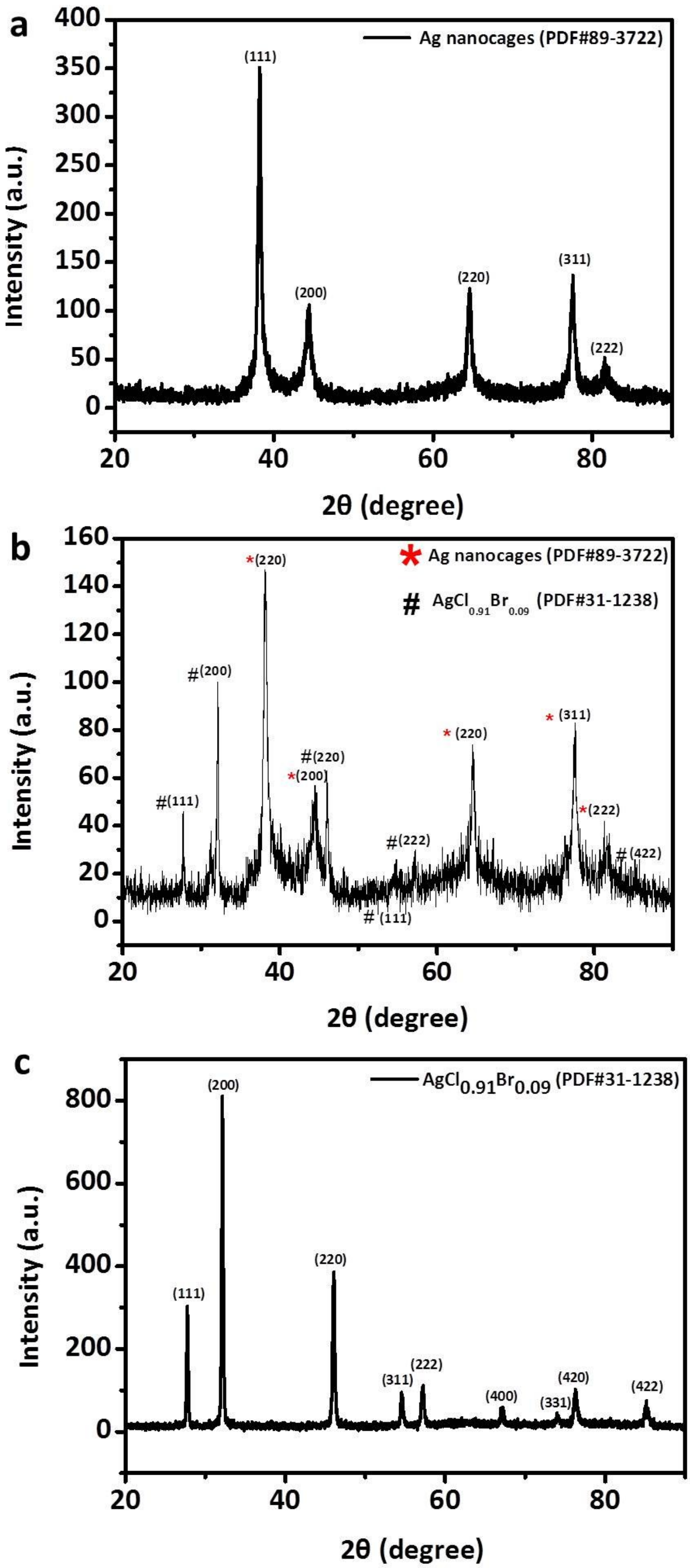

Figure S7 XRD patterns of the nanostructures synthesized with different concentration of $NaBH_4$: (a) 0.1 M, (b) 0.05 M, and (c) 6.2 $*10^{-3}$ M, respectively.

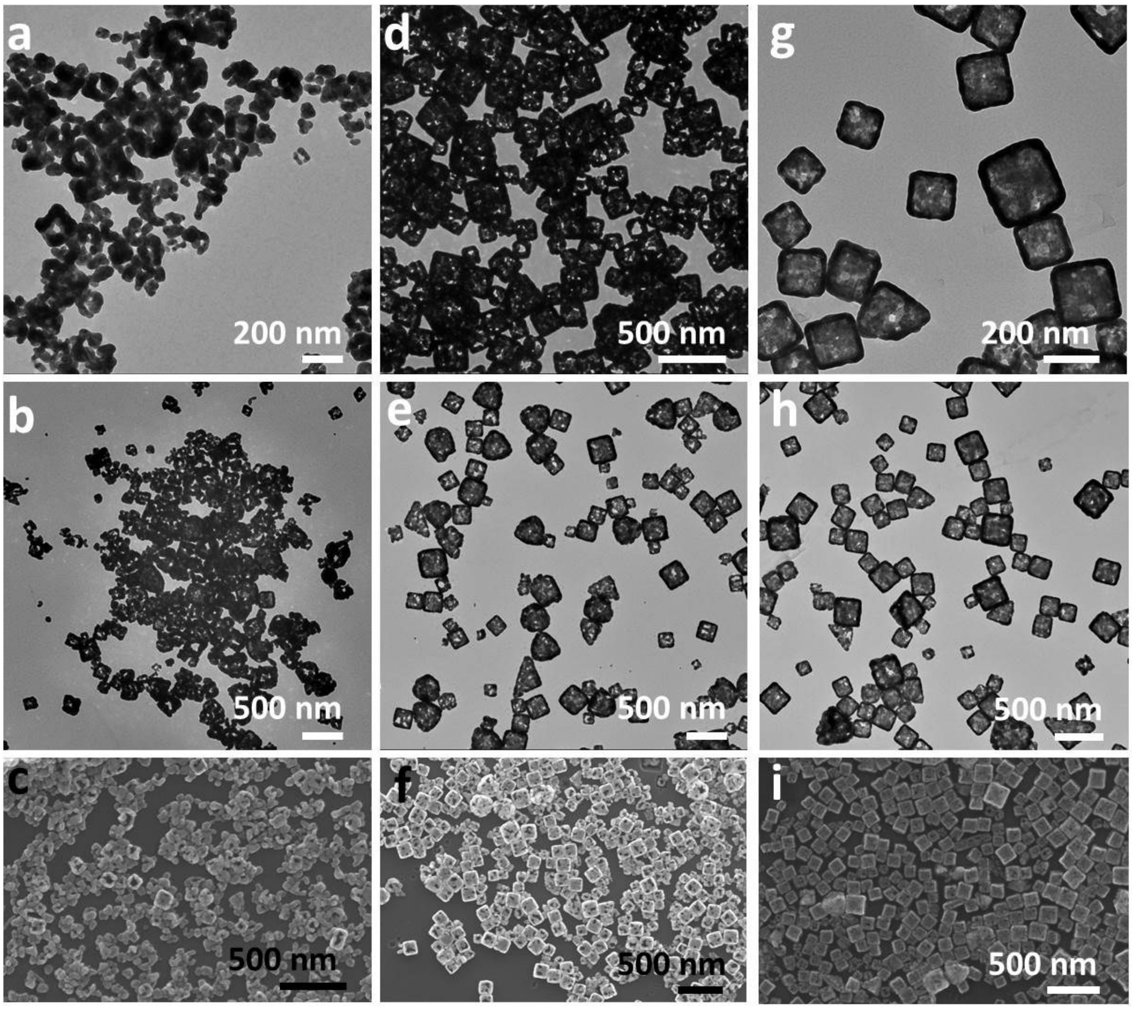

Figure S8 TEM and SEM images of the Ag nanostructures synthesized with different concentration of PVP: (a-c) 0 M, (d-f) 0.24 M, and (g-i) 1 M, respectively.

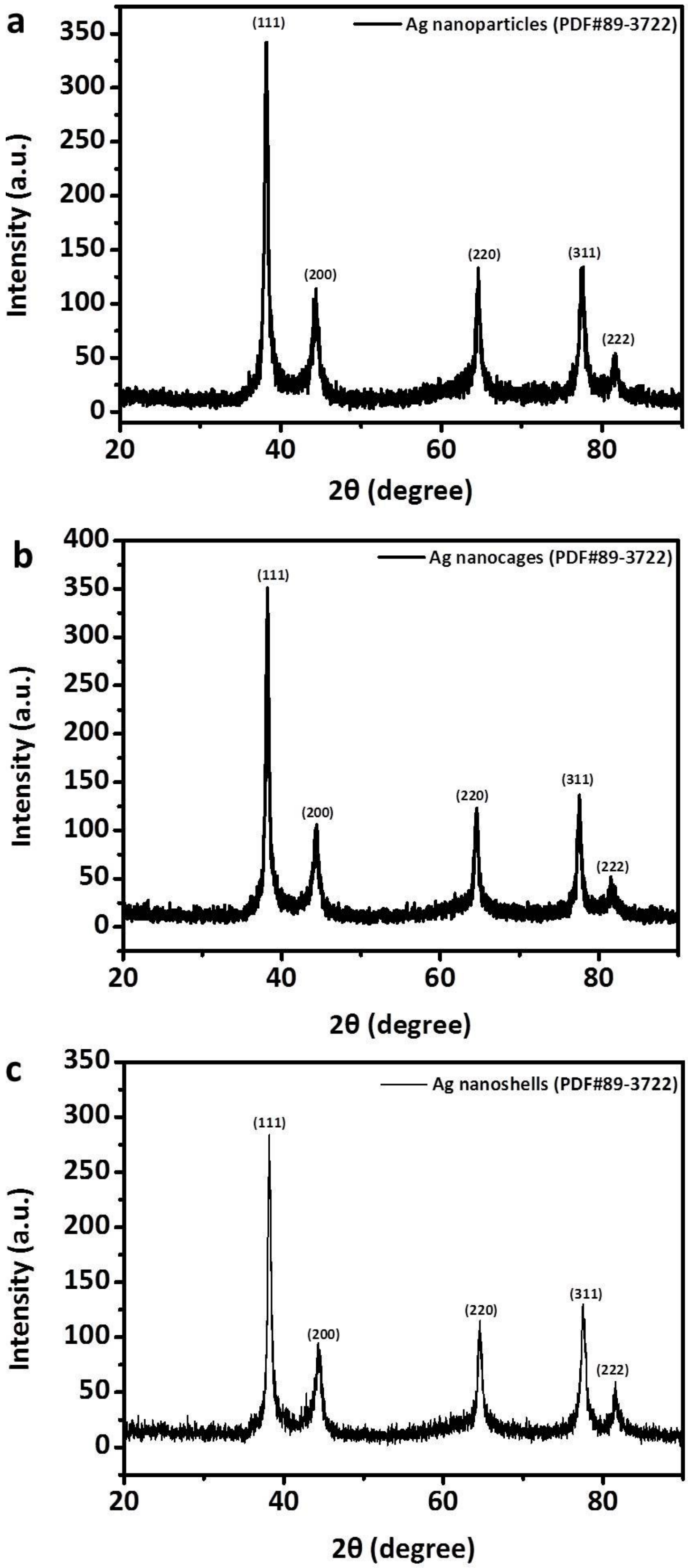

Figure S9 XRD patterns of the Ag nanostructures synthesized with different concentration of PVP: (a) 0 M, (b) 0.24 M, and (c) 1 M, respectively.

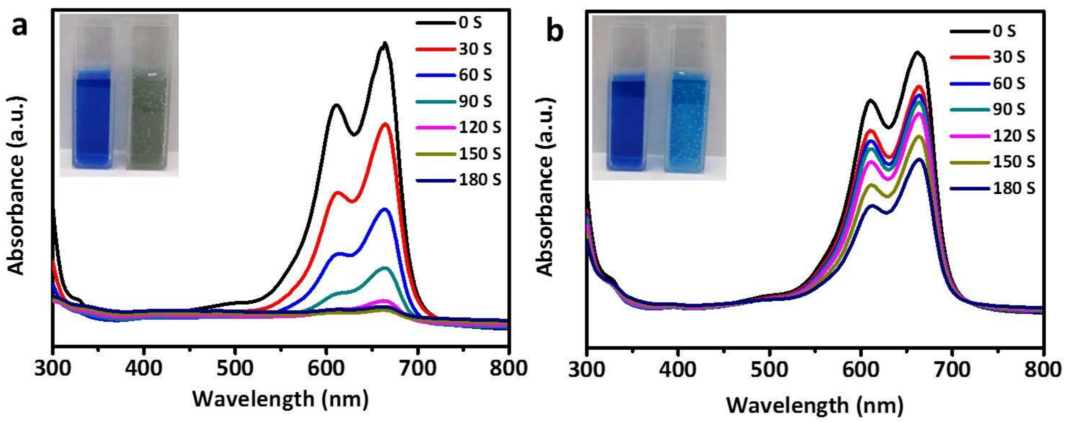

Figure S10 Time-dependent UV-Vis absorption spectra of reduction of MB by (a) Ag nanoframes, and (b) Ag nanoparticles.

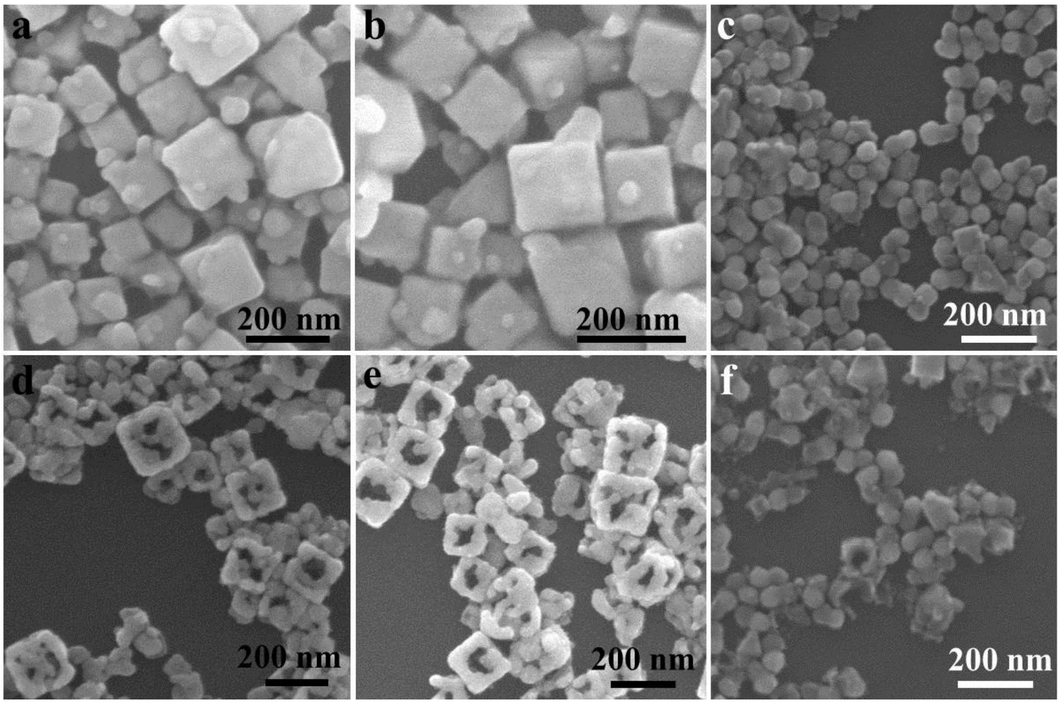

Figure S11 SEM images of (a) AgCl nanocubes, (b) $AgCl_{0.77}Br_{0.23}$ nanocube, and (c) AgBr nanoparticles used as templates; (d-f) The resulting products of (a), (b), and (c), respectively. .

References:

1. Z. Li, J. S. Okasinski, D. J. Gosztola, Y. Ren and Y. Sun, *J. Mater. Chem. C*, 2015, **3**, 58-65.

2. a) Y. Feng, J. He, H. Wang, Y. Y. Tay, H. Sun, L. Zhu and H. Chen, *J. Am. Chem. Soc.*, 2012, **134**, 2004-2007; b) G. Frens, *Nat. Phys. Sci.*, 1973, **241**, 20-22.

3. a) Y. Hao, N. Zhang, J. Luo and X. Liu, *Nano*, 2018, **13**, 22-34; b) F. Yang, B. Wang, H. Su, S. Zhou and Y. Kong, *J. Alloys. Compd.*, 2017, **719**, 30-41.