

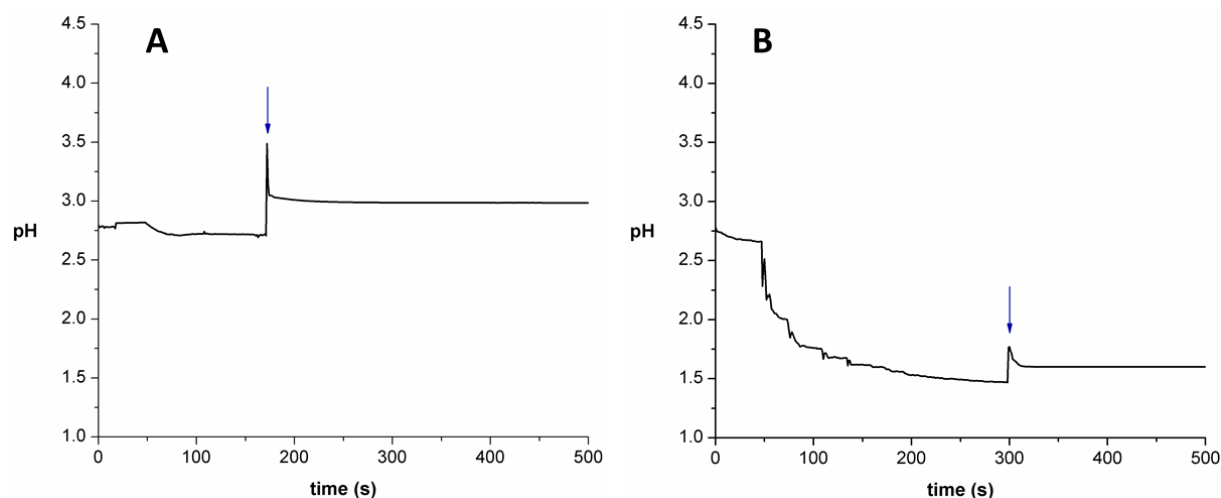
## Electronic Supplementary Information

### Precipitation of Silver Particles with Controlled Morphologies from Aqueous Solutions

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#### A. Continuous measurements of pH during experiments



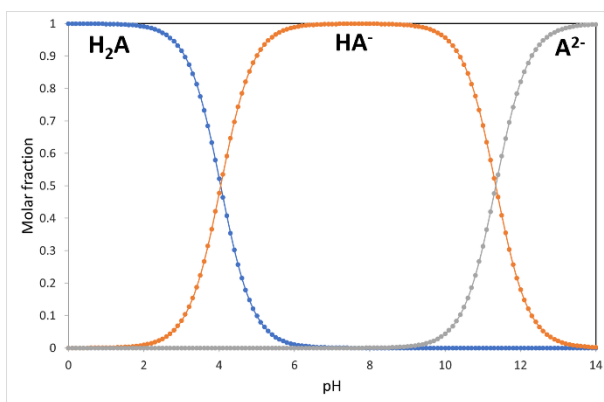
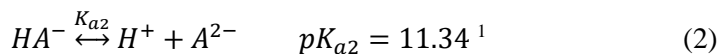
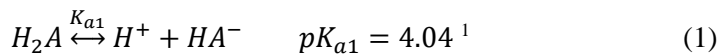
**Figure S1.** Continuous measurements of pH of the AA solutions during (A)  $\text{AgNO}_3/\text{AA} = 20 \text{ mM}/100 \text{ mM}$ ,  $\text{pH}_{\text{AA}} = 2.59$  and (B)  $\text{AgNO}_3/\text{AA} = 10 \text{ mM}/100 \text{ mM}$ ,  $\text{pH}_{\text{AA}} = 1.5$ . Arrows show the time point for the addition of  $\text{AgNO}_3$  to the reaction media.

Figure S1A corresponds to  $\text{AgNO}_3/\text{AA} = 20 \text{ mM}/100 \text{ mM}$ ,  $\text{pH}_{\text{AA}} = 2.59$ , where no pH adjustment was made on the AA solution. It can be seen that the pH is stable until the addition of the silver precursor. A pH increase occurs with the addition of  $\text{AgNO}_3$  solution, which then quickly dropped as a result of the fast redox reaction and stabilized.

Figure S1B corresponds to  $\text{AgNO}_3/\text{AA} = 10 \text{ mM}/100 \text{ mM}$ ,  $\text{pH}_{\text{AA}} = 1.5$ , which was adjusted via slow addition of  $\text{HNO}_3$  in the time interval between 50-200 seconds. Following its adjustment, pH is rather stable until the addition of  $\text{AgNO}_3$  solution.

## B. Oxidation and dissociation reactions of ascorbic acid

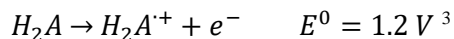
Ascorbic acid is a weak acid and a reducing agent that can lose two protons and two electrons, respectively. The dissociation constants of ascorbic acid in aqueous solution at 25°C are:



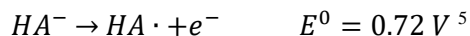
**Figure S2.** The dissociation products of ascorbic acid as a function of pH. The curves were constructed by using the widely tabulated dissociation constants of L-ascorbic acid:  $pK_{a1} = 4.04$  and  $pK_{a2} = 11.34$ .

According to Equations 1 and 2, ascorbic acid ( $H_2A$ ), ascorbate monoanion ( $HA^-$ ) and ascorbate dianion ( $A^{2-}$ ) can be present in aqueous solution depending on the pH of the medium. Different species dominating the solution speciation in accordance to the pH of the solution as shown in Figure S2, lead to different oxidation routes of ascorbic acid.

At low pH when  $H_2A$  is the dominating species<sup>2, 3</sup>;



At moderate pH when  $HA^-$  is the dominating species;

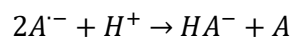


At high pH when  $A^{2-}$  is the dominating species;

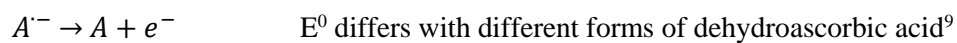


Ascorbic acid commonly functions as a one-electron reducing agent because the ascorbate radical ( $A^{\cdot-}$ ), the one-electron oxidation product of ascorbic acid, is relatively unreactive to non-radical species and reacts preferentially with itself (disproportionation reaction) and other radicals.<sup>6, 7</sup> However, the ascorbate radical ( $A^{\cdot-}$ ) has also been reported as an active reducing agent during the reduction of 2,6-dichlorophenolindophenol (DCIP) and ferricyanide by ascorbic acid.<sup>8</sup> Both the disproportionation reaction and the oxidation of ascorbate radical ( $A^{\cdot-}$ ) produce dehydroascorbic acid ( $A$ ) as following, the fully oxidized form of ascorbic acid, frequently denoted as DHA in literature.

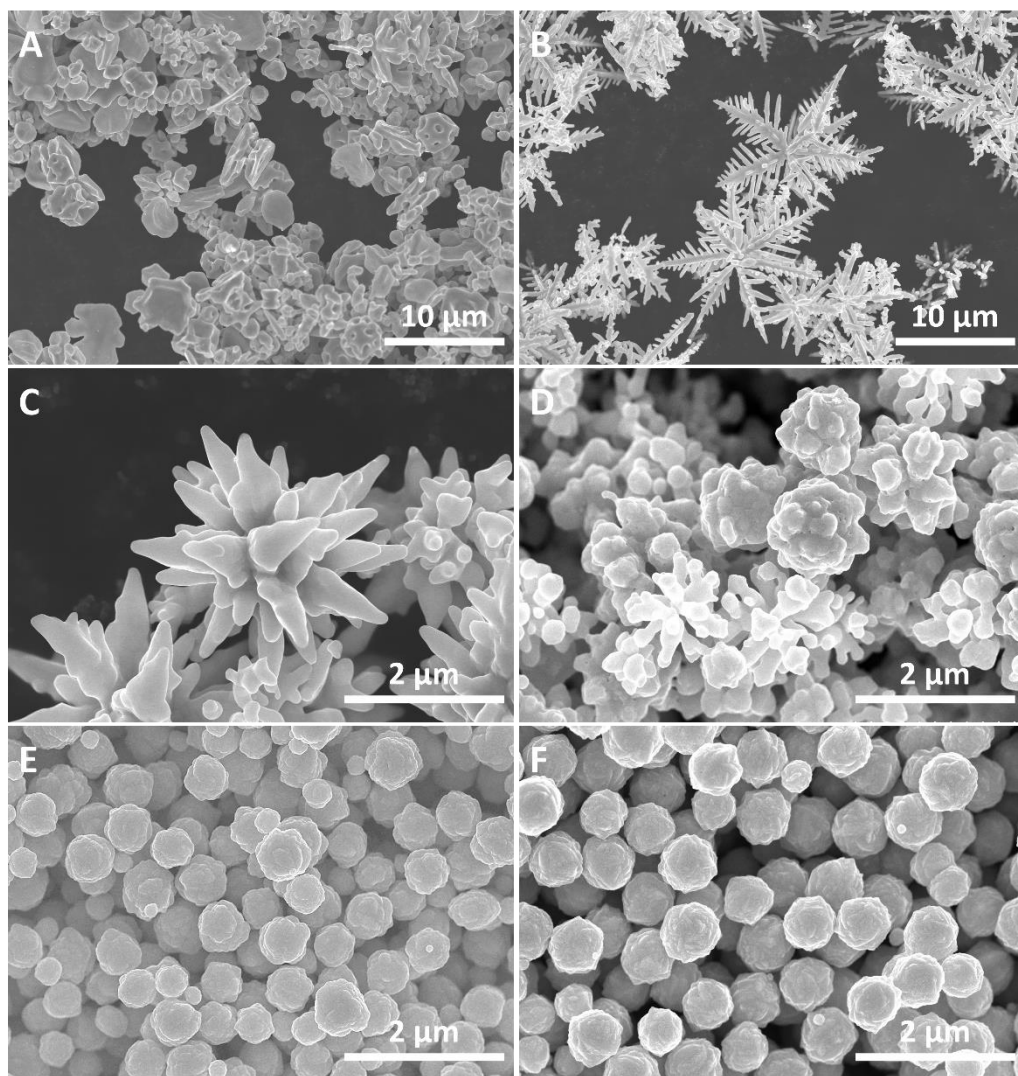
Disproportionation reaction of ascorbate radical ( $A^{\cdot-}$ ):



Oxidation of ascorbate radical ( $A^{\cdot-}$ ):

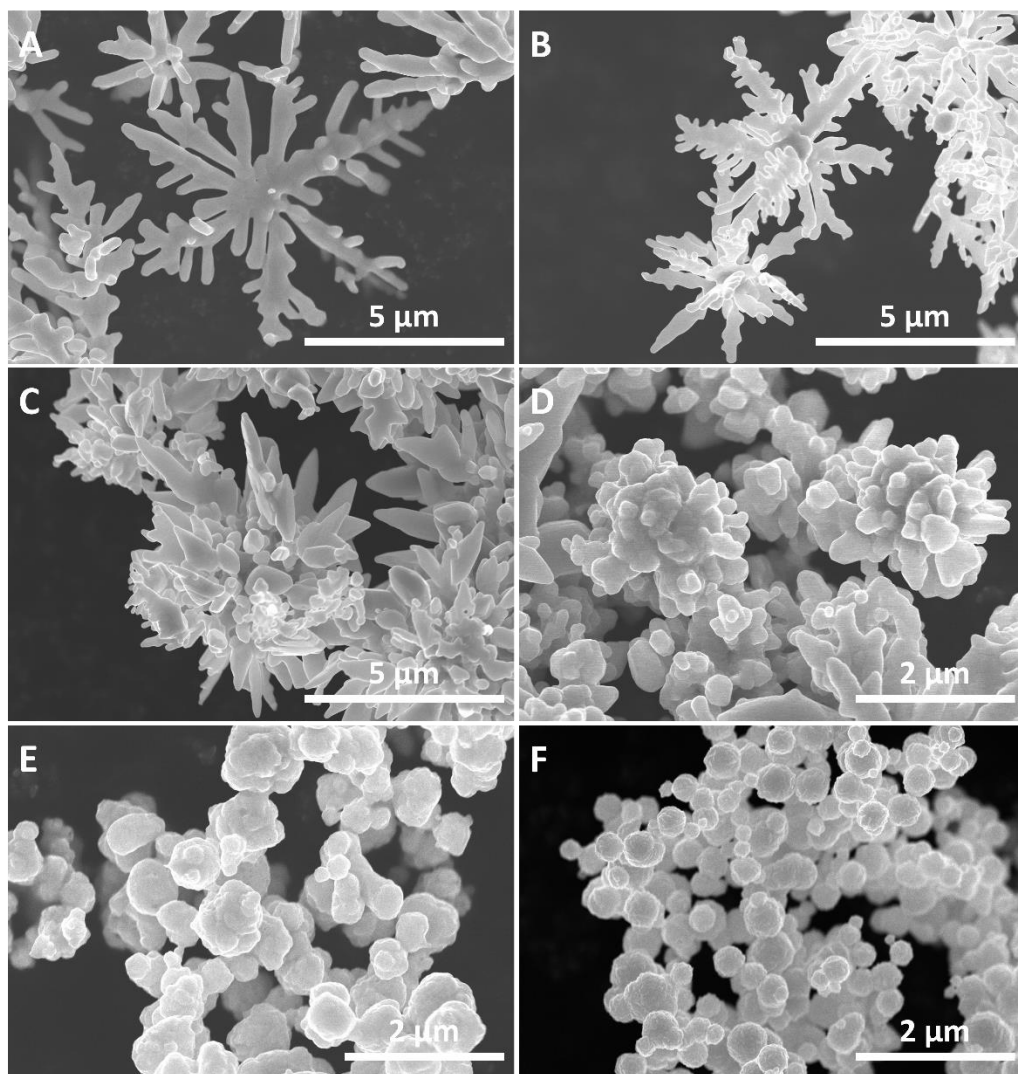


**C. SEM images of silver particles formed at  $\text{AgNO}_3/\text{AA} = 10 \text{ mM}/50 \text{ mM}$  (experiment series 2)**



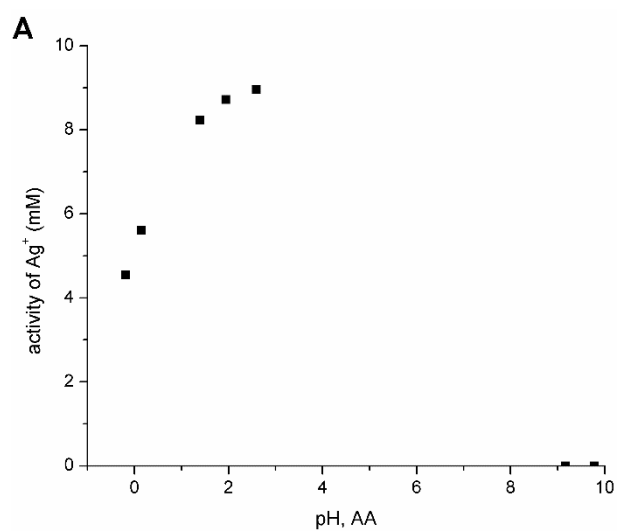
**Figure S3.** SEM images of silver particles formed at  $\text{AgNO}_3/\text{AA} = 10 \text{ mM}/50 \text{ mM}$  (experiment series 2), where initial pH of the AA solution was varied as: (A) 0.65, (B) 1.50, (C) 2.05, (D) 3.56, (E) 9.27, and (F) 10.01.

**D. SEM images of silver particles formed at  $\text{AgNO}_3/\text{AA} = 200 \text{ mM}/1000 \text{ mM}$  (experiment series 4)**



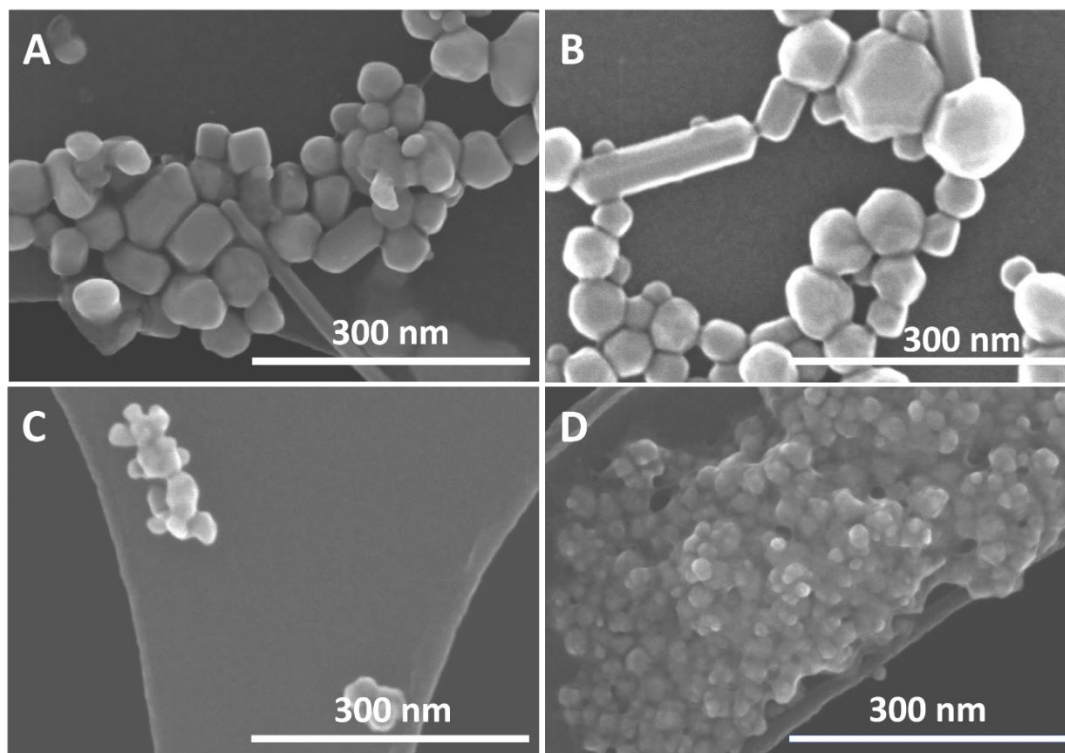
**Figure S4.** SEM images of silver particles formed at  $\text{AgNO}_3/\text{AA} = 200 \text{ mM}/1000 \text{ mM}$  (experiment series 4), where initial pH of the AA solution was varied as: (A) 0.39, (B) 1.06, (C) 2.01, (D) 2.30, (E) 4.04, and (F) 10.13.

### E. Thermodynamic calculations of the silver ion activity in solution



**Figure S5.** Thermodynamic calculations show the activity of the silver ion in solution at  $\text{AgNO}_3/\text{AA} = 20$  mM/100 mM and varying pH, assuming conditions prior to reduction in solution.

**F. SEM images of silver particles formed at low reactants concentration, where the pH was adjusted with NaOH**



**Figure S6.** SEM images of silver particles formed at  $\text{AgNO}_3/\text{AA} = 0.1 \text{ mM}/0.5 \text{ mM}$ , where the pH was adjusted with NaOH at different values as: (A) 3.0, (B) 5.0, (C) 10.0, (D) 12.0. Results showed a similar trend in particle morphologies where a change from (A-B) polyhedral particles to (C) spherulitic onset and (D) decreasing particle size was observed with increasing pH.

## References

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