

Electronic supplementary information

***In situ* Studies of Different Growth Modes of Silver Crystals Induced by Concentration Field in Aqueous Solution**

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Experimental

In order to study the effect of concentration profile to crystal growth, a simple and straightforward strategy was developed that was spontaneous galvanic displacement between silver ions and zinc plate. In a typical experiment, a pure zinc plate was immersed into silver nitrate aqueous solution, and spontaneous displacement reaction would happen at the interface between zinc plate and solution. Due to the different redox potential between Zn and Ag, the Ag⁺ was reduced into silver atoms and deposited on the interface to form silver crystal with hierarchical shape. During the reaction, a concentration diffusion field was formed near the reaction interface. The reaction was performed in a quartz glass cell which inner volume was 80 mm × 60 mm × 1 mm (length × width × thickness). Before the reaction, the zinc plate with size of 20 mm × 10 mm × 0.8 mm (length × width × thickness) was treated with diluted hydrochloric acid to remove surface dirt and oxide. The Zn plate was immersed in dilute hydrochloric acid (5 mM) for 10 Min and then washed several times using de-ionized distilled water.

The morphologies of the hierarchical silver crystals were *in situ* monitored using a CCD (charge-coupled device) camera with $\times 200$ lens which was settled vertically on the reaction cell. Similarly with other's report,¹ the concentration map near the reaction interface was measured using a Michelson interferometer and *in situ* recorded using a CCD camera with $\times 10$ lens. To study the evolution of silver hierarchical crystal shapes in different silver ions concentration solutions, three concentrations were used: 30 mM, 100 mM, and 200 mM. The solution pH values are 5.29, 5.18 and 5.06 separately for these three concentrations. The crystal phase of as-prepared silver trees on zinc plate was characterized by an X-ray diffractometer (Bruker-AXS D8 ADVANCE) using Cu-K α radiation ($\lambda=1.54\text{\AA}$) in the range of $5-90^\circ 2\theta$. The morphology and elements of the products was investigated by field-emission scanning electron microscopy (FE-SEM) using JEOL (JSM-7000F) at an accelerating voltage of 20kV. The silver hierarchical crystals were separated from zinc plate by sonicate in ethanol solution. Then they were dropped on copper grid and characterized with a JEOL JEM-2100 transmission electron microscope operating at an accelerating voltage of 200kV.

Figures and captions

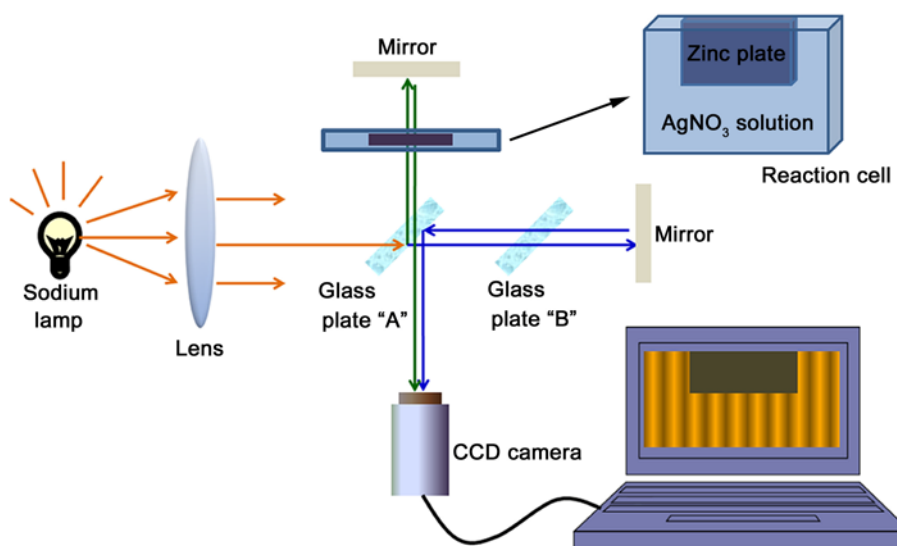


Fig. S1 Schematic sketch to illustrate the *in situ* measurement of concentration profile near reaction interface. Glass

plate "A" is half-reflect glass and through it, about one-half of incidence light will be reflected by one of this glass.

Glass plate "B" is used to compensate optical path difference.

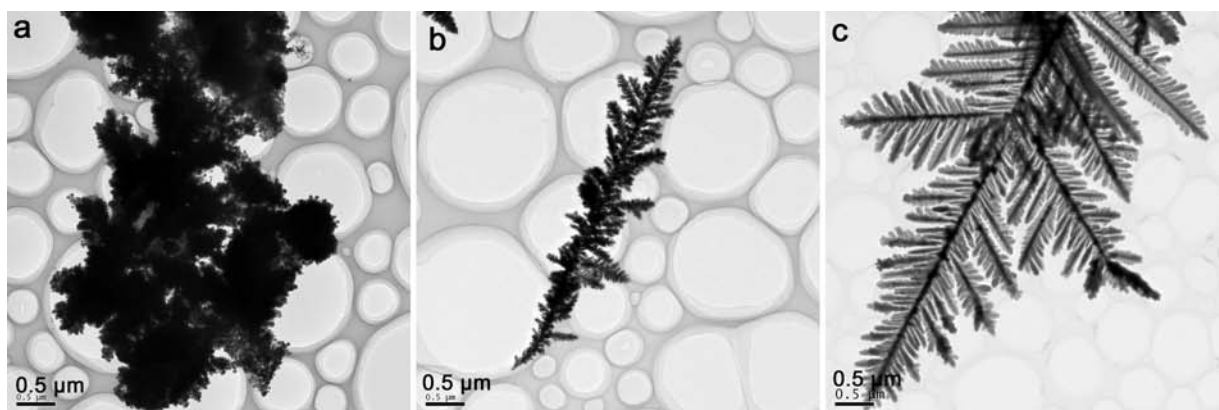


Fig. S2 TEM images of silver hierarchical crystals grown on zinc plate at different silver ion concentrations: (a) 30 mM, (b) 100 mM, and (c) 200 mM.

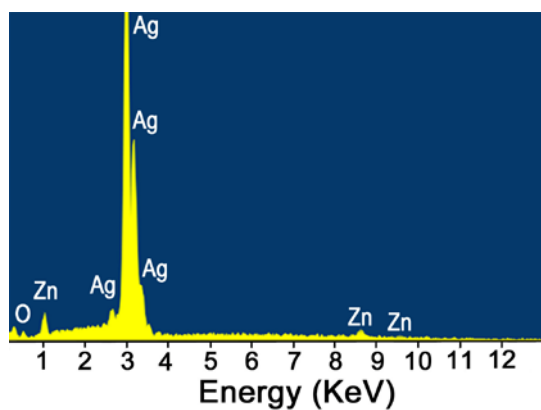


Fig. S3 Scanning electron microscope-energy dispersive X-ray (SEM-EDX) analysis of silver hierarchical crystals grown on zinc plate at silver ion concentrations of 100 mM.

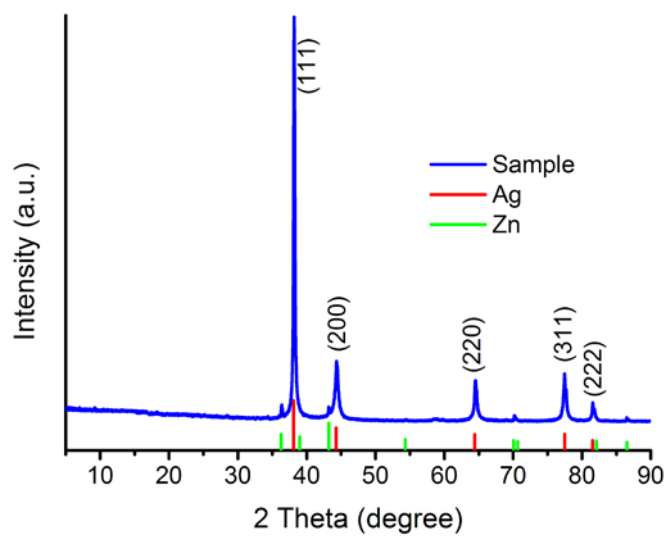


Fig. S4 X-ray diffraction (XRD) patterns of silver hierarchical crystals grown on zinc plate at silver ion concentrations of 100 mM.

References

- 1 You, H. J.; Fang, J. X.; Chen, F.; Zhu, C.; Song, X. P.; Ding, B. J., *Chem. Phys. Lett.* **2008**, *465*, 131-135.