

Supporting Information

Charge Gradient-Induced On-Surface Growth of Ultralarge Single-crystalline Ag Nanomembranes for Long Surface Plasmon Propagation

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Experiment in detail

Materials.

AgNO₃ (ACS, 99.9+%, Alfa), ethylene glycol (AR, Sinopharm Chemical Reagent Co., Ltd), ethyl alcohol absolute ($\geq 99.7\%$, Sinopharm Chemical Reagent Co., Ltd), NaOH (AR, Sinopharm Chemical Reagent Co., Ltd), (NH₄)₂S₂O₈ (98%, Alfa) were used as received. Millipore purified water was used in all the experiment.

Synthetic Procedures.

Synthesis of Cu(OH)₂ nanowire-haired copper mesh: The commercial copper meshes with a mesh number of 500 were ultrasonicated in deionized water to remove contaminants before use, and then immersed in an aqueous solution of 2.5 M NaOH and 0.13 M (NH₄)₂S₂O₈ at room temperature for reaction for 35 min. The membranes were taken out and washed with deionized water repeatedly.

Synthesis of single-crystalline Ag NMs on nanowire-haired copper mesh: A piece of nanowire-haired copper mesh (1 cm×1 cm) was dipped into silver nitrate solution (2.5 mM) with a small amount of ethylene glycol (100 μ l). One day later, the surface of membrane turned white and the solution became to be light blue. The products on the surface can be peeled from by mild ultrasonic and washed repeatedly with water and ethanol for 3 times in a centrifugal way, respectively.

Preparation of vacuum-deposited Ag film: A poly-crystalline Ag film with thickness of ~ 50 nm was deposited on the silicon by magnetron sputtering. The argon flow rate for the sputtering of film was 20 sccm. Before the deposition of Ag, a poly-crystalline

chromium (Cr) film with thickness of 10 nm as an adhesive layer was sputtered firstly at the working volt, electric current, power of 330 V, 1.51 A, 0.5 kW, respectively. The poly-crystalline Ag film was sputtered on the Cr film at the working volt, electric current, and power of 475 V, 1.05 A, 0.2 kW, respectively.

Focused ion beam (FIB) milling: A dual-beam FEI Quanta 200 3D FIB workstation was used for the FIB milling on both single-crystalline Ag nanomembrane and deposited Ag film. The patterns with periodicity of 700 nm were etched using 30 kV as the acceleration voltage and 100 pA as the ion-beam current. The approximate spot size was 25 nm.

Characterization.

Scanning electron microscopy (SEM) images were obtained on a field-emission scanning electron microscope (Hitachi S4800, Japan). Transmission electron microscopy (TEM) was measured on a Tecnai G2 F20 S-Twin field-emission transmission electron microscope. X-ray Diffraction was collected on a Bruke D8. Atomic Force Microscopy (AFM) was obtained on a Dimension 3100, Veeco. Optical microscopy images were obtained on an OLYMPUS BX51. Contact angles were measured on an OCA20 machine (Data-physics, Germany). Cathodoluminescence (CL) test was conducted on Quanta 400 FEG and Mono CL 3+.

1. Characterization of nanowire-haired copper mesh

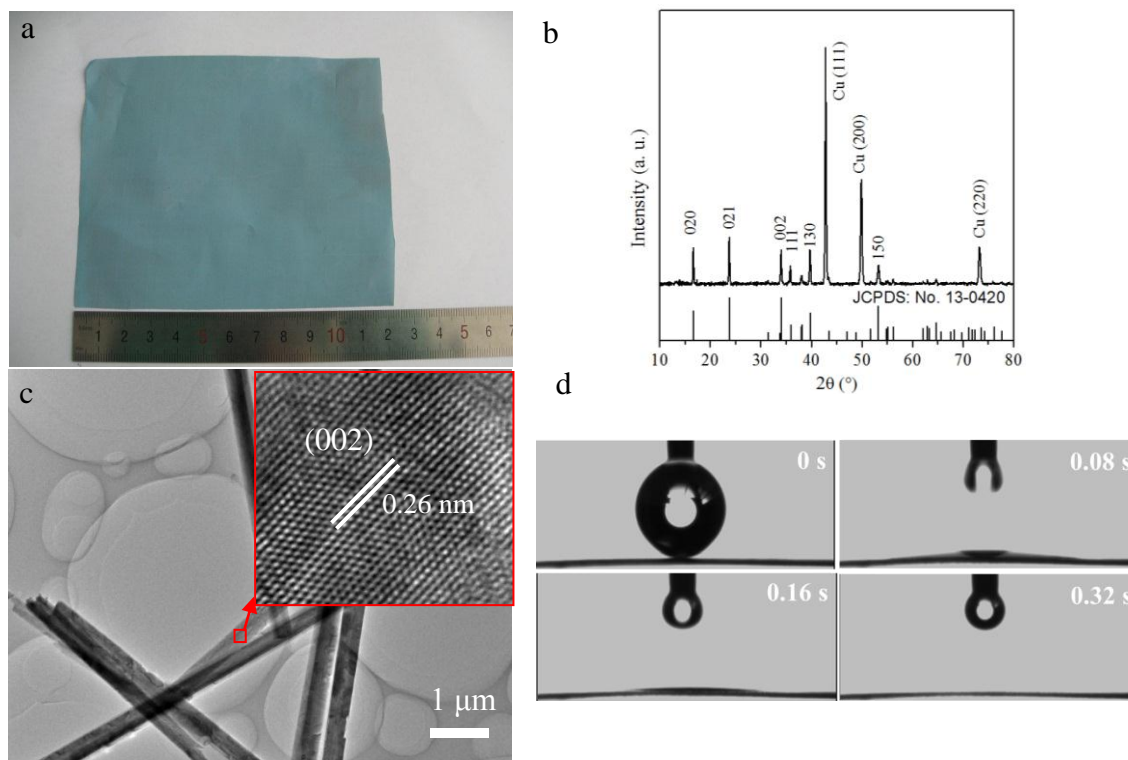
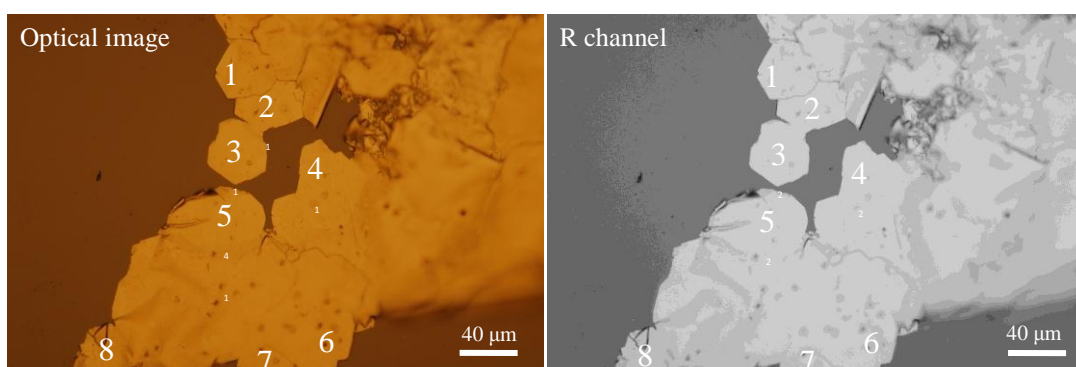


Figure S1. Structural characterization of $\text{Cu}(\text{OH})_2$ nanowire-haired membrane. (a) Photograph of a large-scale nanowire-haired membrane. (b) XRD pattern of the membrane. (c) TEM image of nanowires from the membrane (inset: HRTEM image of a nanowire). (d) Figure 1d. Spreading and permeating behavior of a water droplet on nanowire-haired copper mesh. A water droplet could completely wet the membrane within 0.32 s.

2. Optical microscopy imaging and thickness identification using image J software

Due to the large area of our samples, it is not a good way to use AFM to give a thickness-distribution. A method using optical image and software proposed by Zhang to make statistics analysis with the thickness of nanosheets can overcome this problem, which has been demonstrated in the large area nanosheets in the previous work.^{1,2} The detail experiment is as follows: an optical microscopy was used to

capture the samples which were dispersed on the silicon wafer. Then the color optical images were opened by the software of Image J. The R channel of the image could be extracted by the following steps: “Image>Color>Split Channels” in the menu. A line was drawn across the Ag membrane in the grayscale image, and the line profile of intensity difference was obtained by pressing “Ctrl + K”. The intensity values can be shown when clicking “List” button. As we reported, the intensity values have a good line relationship with the values of thickness. Therefore, whole statistics of thickness in the samples can be obtained using method. The thickness of membranes is in the range of 53 ± 3 nm.



No. of membranes	1	2	3	4	5	6	7	8
Gray value	75	78	79	80	81	83	80	75
Thickness (nm)	50	52	53	54	55	56	54	50

Figure S2 and Table S1. Optical identification of Ag NMs using software of Image J and thickness summary corresponding to the optical image.

3. Zeta potential of $\text{Cu}(\text{OH})_2$ nanowires

The $\text{Cu}(\text{OH})_2$ nanowires were peeled off from the copper mesh firstly by gentle ultrasonification. The obtained nanowires were redispersed into water for measurement of zeta potential.

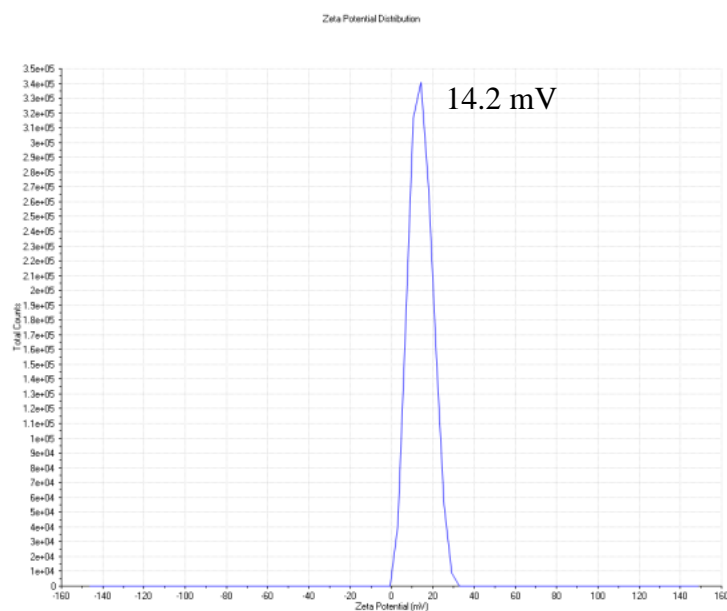


Figure S3. Zeta potential of $\text{Cu}(\text{OH})_2$ nanowires in water.

In order to further prove our mechanism, metal salt with negative charge (for example, AuCl_4^-) was introduced into the system including a piece of nanowire-haired copper mesh flatting at the bottom. The other experiment condition was same as that used in the main text. After for one day, the membrane was rinsed with deionized water and ethanol for 3 times, respectively, used for further characterization. As shown in Figure S4, the Au nanostructures can only be found around the nanowire surfaces but not on nanowire surfaces. It is attributed to the electrostatic attraction between nanowires and AuCl_4^- ions.

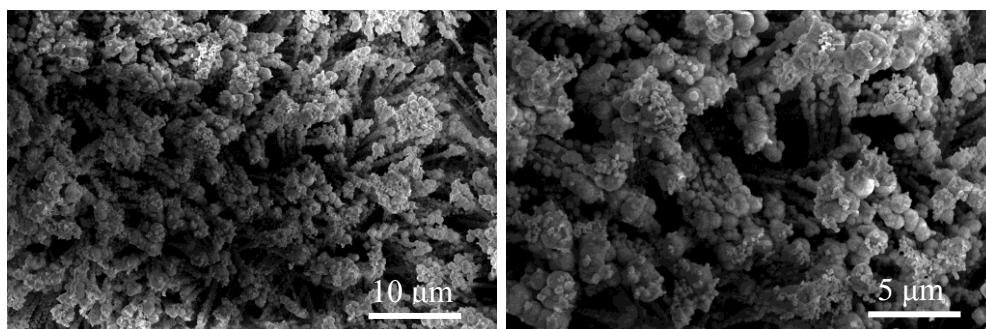


Figure S4. SEM images of products obtained using AuCl_4^- as the source material.

4. Control experiment to prove the role of ethylene glycol as capping agent

In order to prove the role of ethylene glycol on growth of Ag NMs, a control experiment was done where ethylene glycol was absent and other experiment conditions were same as that used in the main text. The detail experiment is as follows: The inorganic membrane ($1\text{ cm} \times 1\text{ cm}$) composed of copper skeleton wrapping up with $\text{Cu}(\text{OH})_2$ nanowires was dipped into silver nitrate solution (2.5 mM). One day later, the surface of membrane turned white. The products on the surface can be peeled away from the membrane by mild ultrasonic and washed repeatedly with water and ethanol for 3 times in a centrifugal way, respectively. As shown in Figure S5, no membranes were produced except large Ag dendritic nanostructures. This result indicates the role of ethylene glycol in the growth of Ag NMs as capping agent.

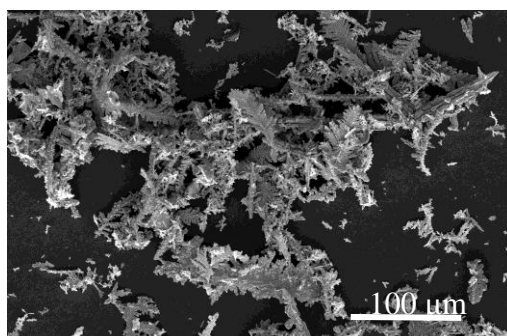


Figure S5. Products obtained when the reaction was processed in the absence of ethylene glycol.

5. AFM images of Ag nanomembrane and deposited Ag film.

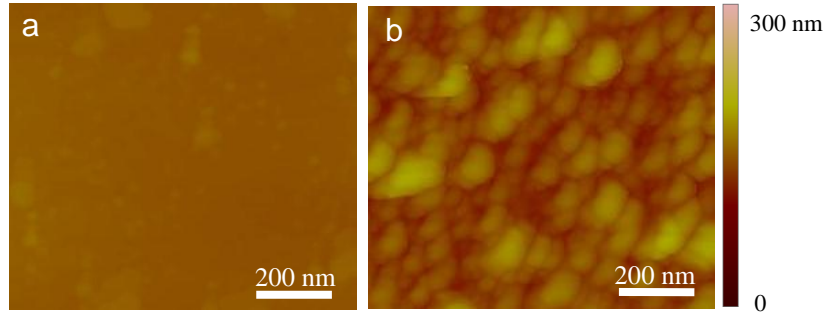


Figure S6. AFM images of the Ag nanomembrane (a) and deposited Ag film (b) recorded apart from the patterned area.

6. Propagation length of surface plasmon polaritons (SPPs):

The approach for the measurement of SPP propagation length was done according to previous reports.³ A 30 keV electron beam from FEI SEM with a beam diameter of around 5 nm was used to excite SPPs on both FIB-patterned Ag membrane and deposited Ag film. The out-coupled light was collected by a optical microscope placed over the sample. With focusing the electron beam, scattering spectra were collected with changing the distance from electron beam to grating pattern. The scattered intensity at each wavelength λ , $I(d, \lambda)$, was fitted to the following equation:

$$I(d, \lambda) = I_0(\lambda) e^{-d/L_{\text{SPP}}(\lambda)} + I_b(\lambda),$$

where $I_0(\lambda)$ is the SPP intensity at the grating pattern, $L_{\text{SPP}}(\lambda)$ is the SPP propagation length, and $I_b(\lambda)$ is the background intensity.

7. Control experiment to prove the role of necessity of Cu(OH)₂ nanowires in the preparation of Ag NMs

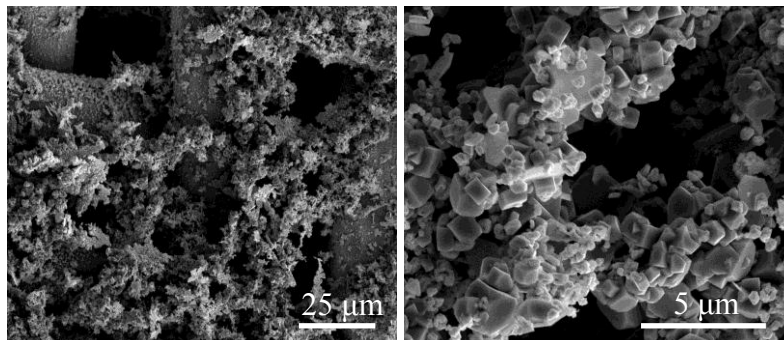


Figure S7. SEM images of a control experiment by adding ethylene glycol alone on top of the copper mesh without Cu(OH)₂ nanowires.

Supplementary references:

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2. Qin, H. L.; Wang, D.; Huang, Z. L.; Wu, D. M.; Zeng, Z. C.; Ren, B.; Xu, K.; Jin, J. *J. Am. Chem. Soc.* **2013**, *135*, 12544.
3. van Wijngaarden, J. T.; Verhagen, E.; Polman, A.; Ross, C. E.; Lezec, H. J.; Atwater, H. A. *Appl. Phys. Lett.* **2006**, *88*, 221111.