Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Water-Mediated Polyol Synthesis of Pencil-like Sharp Silver Nanowires Suitable for Nonlinear Plasmonics

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1. Silver nanowire Synthesis

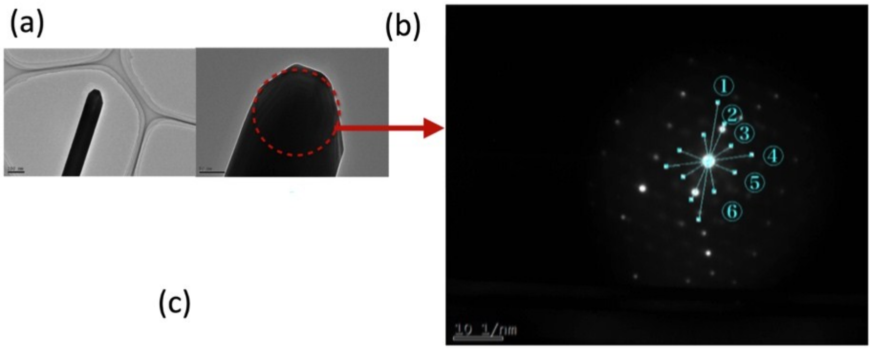
Silver nitrate ($AgNO_3$) and ethylene glycol (EG) were purchased from Sigma-Aldrich. Polyvinylpirrolidone K30 (PVP) and copper chloride ($CuCl_2$) were purchased from FUJIFILM wako pure chemical industries, Ltd. All the chemicals were used without further purification. Milli-Q water (18 MΩ•cm, Milli-Q System, Millipore) was used in all the synthesis.

Typical synthesis of silver nanowires has been performed by following the protocol reported by Y. Xia *et al.* (2008).[1] Briefly, 9.66 mL of EG were refluxed with 115.8mg of PVP (0.108 M) at 160 °C for 1 hr. 80 μL of $CuCl_2$ EG solution (4 mM) was then added to this solution followed by adding 100 μL of $AgNO_3$ EG solution (0.12 M) and stirring for another 10 min. After the solution color turns greenish, 4.9 mL of $AgNO_3$ EG solution (0.12 M) was added drop-wise with an injection rate of 100 μL / 1 min. After adding the $AgNO_3$ solution, the reaction mixture was further refluxed at 160 °C typically for 1 hour. Magnetic stirring was applied throughout the entire process. After the reaction, the mixture was cooled down to room temperature under ambient condition. After the process, the mixture was washed with ethanol by centrifuged the solution 3 times at 1200 rpm for 10min to remove excess amount of PVP, EG and any other chemicals. Finally, the precipitated AgNWs were dispersed in ethanol. For the investigation of the effect of milli-Q during the reaction, small amount of milli-Q water were added in EG during the synthesis. All the solution preparation and synthesis were performed at humidity of ~ 20%. Note that appropriate amount of water to produce sharp AgNWs has to be determined on each lot of anhydrous EG, because each lot contains different trace amount of water. However, the appropriate amount of water can be usually found around 0.2 ~ 0.5 v/v%.

The morphology of AgNWs was characterized by means of field emission scanning electron microscopy (FE-SEM) (JEOL JSM-6700FT field-emission scanning electron microanalyzer at an accelerating voltage of 5 kV).

2. Transmission Electron Microscopy (TEM) and diffraction patterns

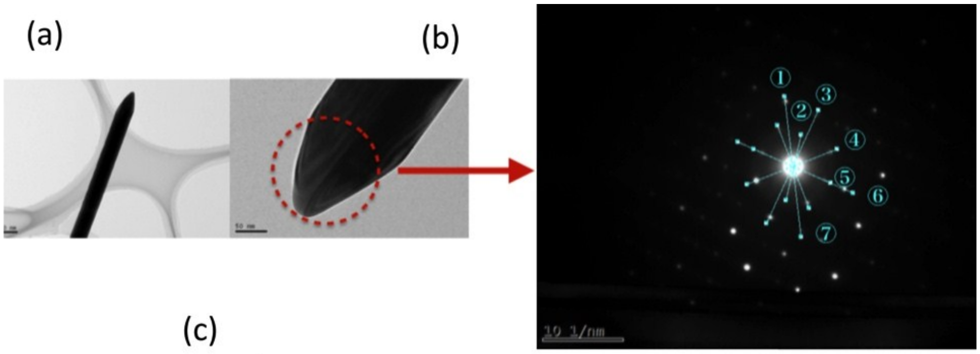
TEM measurements were conducted by means of JEM-2100F (JEOL) accelerating voltage of 200 kV. The diffraction patterns were analyzed based on the face centered cubic (fcc) crystalline structure of metallic silver (JCPDS file no. 00-004-0783).



(c)

	2d [1/nm]	d [1/nm]	d [nm]	hkl
①	21.505	10.753	0.0930	331
②	14.175	7.0875	0.1411	220
③	8.568	4.284	0.2334	111
④	16.06	8.03	0.1245	311
⑤	8.939	4.4695	0.2237	-
⑥	8.573	4.2865	0.2333	111

Figure S1 (a) TEM images of a trapezoid-like end of an AgNW. (b) Diffraction pattern at the end part. (c) A list of facets detected.



(c)

	2d [1/nm]	d [1/nm]	d [nm]	hkl
①	16.4	8.2	0.1220	311
②	7.156	3.578	0.2785	-
③	14.007	7.0035	0.1428	220
④	9.939	4.9695	0.2012	200
⑤	8.5	4.25	0.2353	111
⑥	13.918	6.959	0.1437	220
⑦	9.949	4.9745	0.2010	200

Figure S2 (a) TEM images of a sharp end of an AgNW. (b) Diffraction pattern at the end part. (c) A list of facets detected.

3. SEM images of AgNWs synthesized with different concentration of water in EG

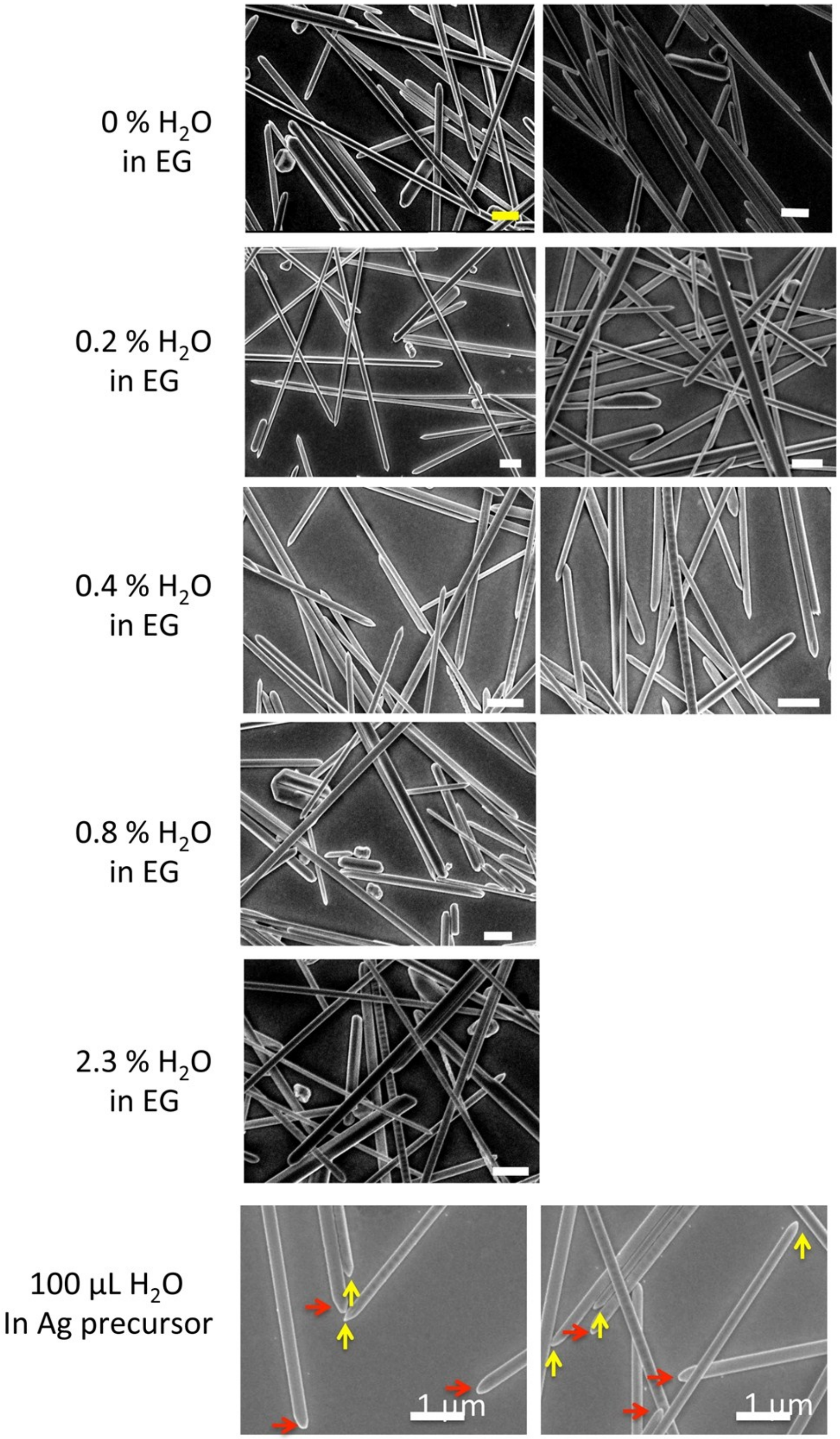


Figure S3 SEM images of AgNWs synthesized in the presence of 0 – 2.3% (v/v) of water in EG and with Ag precursor including 100 µL of water. (Scale bar 1 µm)

4. Table S1 ICP-OES

Inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis (ICPE-9000, SHIMAZU CORPORATION) has been carried out in order to determine concentration of Ag+ in the reaction as function of time.

	2.5 min	10 min	60 min
0%(v/v)	71,25	4,325	5,05
0.4%(v/v)	64,25	5,425	10,725
2.3%(v/v)	66,75	8,125	13,275

(ppm)

5. Table S2 Dependence of amount of water on edge morphology

Amount of H_2O in EG / % (v/v)	Reaction temperature / ˚C	Reaction time after Ag^+ addition / h.	Edge morphology (1) Trapezoid (2) Sharp	Diameter / nm
0	160	1	(1) 100 % (2) 0 %	200 ± 48
0.20	160	1	(1) 8 % (2) 92 %	206 ± 45
0.40	160	1	(1) 10 % (2) 90 %	190 ± 39
0.79	160	1	(1) 40 % (2) 60 %	198 ± 61
2.3	160	1	(1) 70 % (2) 30 %	193 ± 40

6. Table S3 Effect of reaction time on edge morphology

Amount of H_2O in EG / % (v/v)	Reaction temperature / ˚C	Reaction time after Ag^+ addition / h	Edge morphology (1) Trapezoid (2) Sharp	Diameter / nm
0.40	160	0.5	(1) 100 % (2) 0 %	212 ± 40
0.40	160	1	(1) 10 % (2) 90 %	190 ± 39
0.40	160	2	(1) 100 % (2) 0 %	153 ± 28
0.40	160	6	(1) 100 % (2) 0 %	227 ± 53

7. Nonlinear optical measurement and sample preparation

Non-linear optical measurement was conducted on an inverted optical microscope (Nikon, Ti-U) equipped with a piezoelectric stage (P517.3CL, Physik Instrument). Non-linear excitation was performed with the output from a femtosecond laser (Spectra-Physics, MaiTai, 820 nm, 120 fs, 80 MHz). The polarization of the fs excitation light was rotated using λ/2 waveplate. The laser beam was directed by using a dichroic mirror and focused on a sample with an objective lens (Nikon, 100x, oil immersion, NA=1.49). The emission from the sample was collected with the same objective and detected with a CCD camera (Andor, Newton 920, -75 ˚C) equipped with a spectrograph (iHR320, Horiba), where a short-pass filter (ET800SP-2P, Chroma) and a 100 μm pinhole are placed before the entrance of the spectrograph. For SHG imaging in Figure 5a, additional short-pass filters were used (ET750SP 2P, Chroma and FES0450, Thorlabs), while fluorescence excited by SHG in Figure 5b were obtained with a shortpass filter (ET750SP 2P, Chroma) and a long-pass filter (FEL0550, Thorlabs).

The AgNWs are washed a few times and the solvent was replaced with isopropanol. The AgNWs solution was spin-coated on a clean glass coverslip, followed by covering the sample with polyvinylalcohol (PVA) film in order to avoid the refractive index mismatching between glass and air. For fluorescence imaging, Rhodamine 6G was added in PVA film.

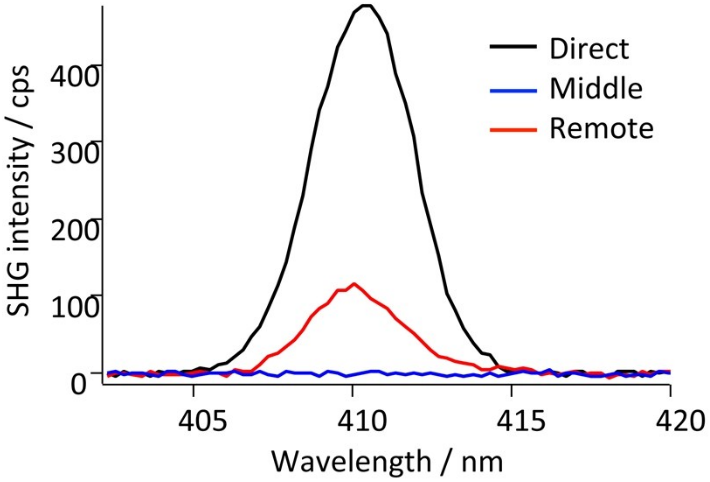


Figure S4 Spectra of SHG at focus point (black line), at the middle (blue line), and at the distal end (red line) with the excitation wavelength of 820 nm (120 fs). SHG are strongly generated with direct excitation, while reasonable intensity is observed with the remote excitation. At the middle of AgNW, SHG was not generated by propagating plasmons.

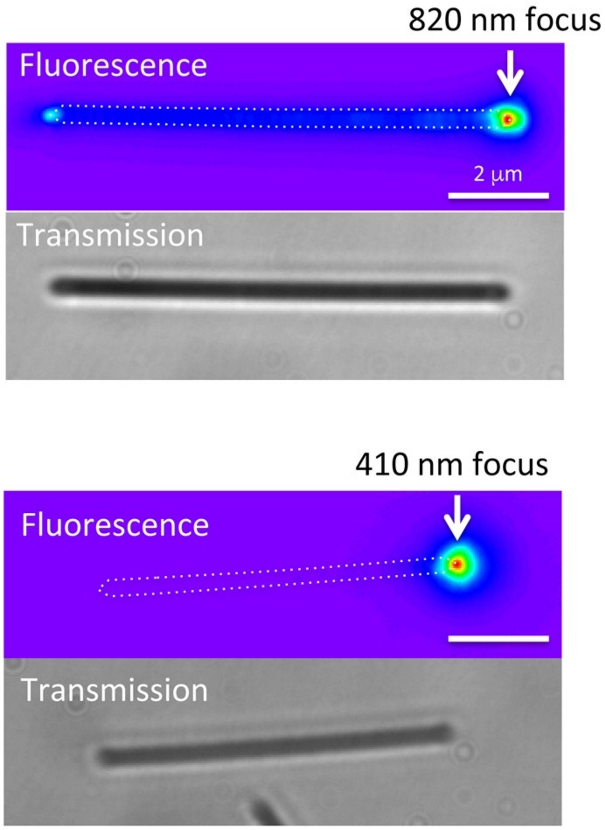


Figure S5 Remote 2-photon excitation of fluorescence at the left end of the AgNWs when excited at the right end with 820 nm (a) and with 410 nm fs laser light (b). Fluorescence was remotely excited with propagating 820nm, while no fluorescence was observed with 410nm, indicating 410 nm light does not propagate along the AgNWs over micrometers.

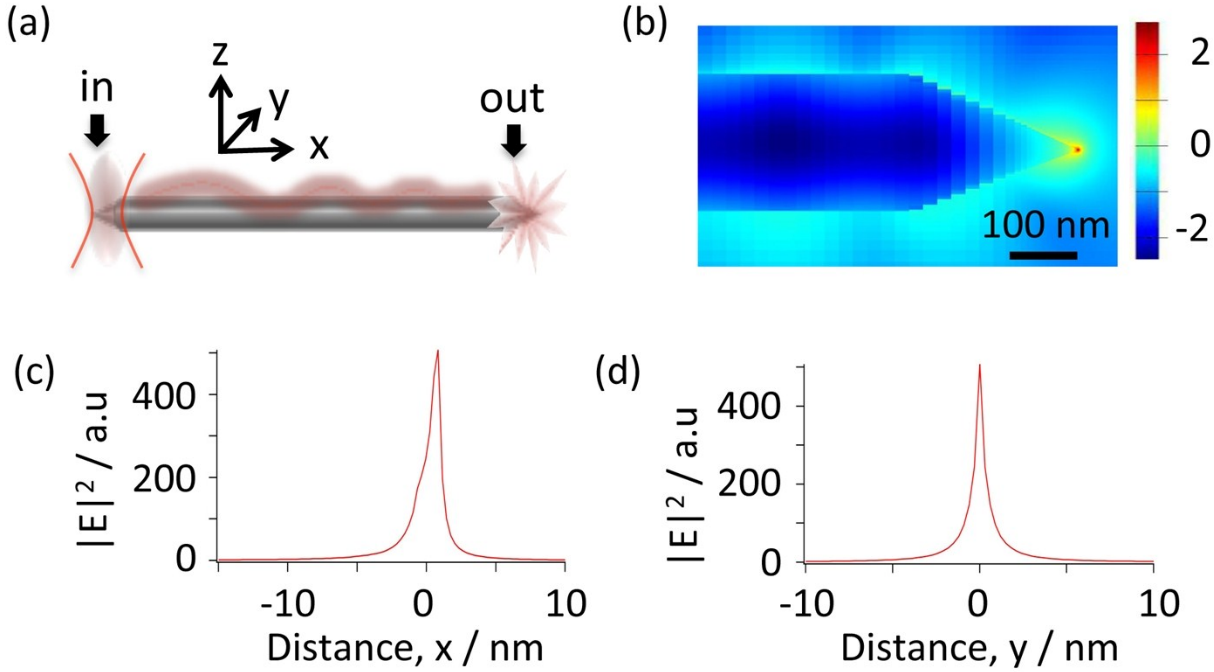


Fig. S6 (a) Configuration of AgNWs for the numerical calculation. (b) Near field EM intensity at the right end of the nanowire, plotted with log$|E^2|$. Line profiles of the EM intensity map in Fig. S11b along x axis (c) and y axis (d), respectively.

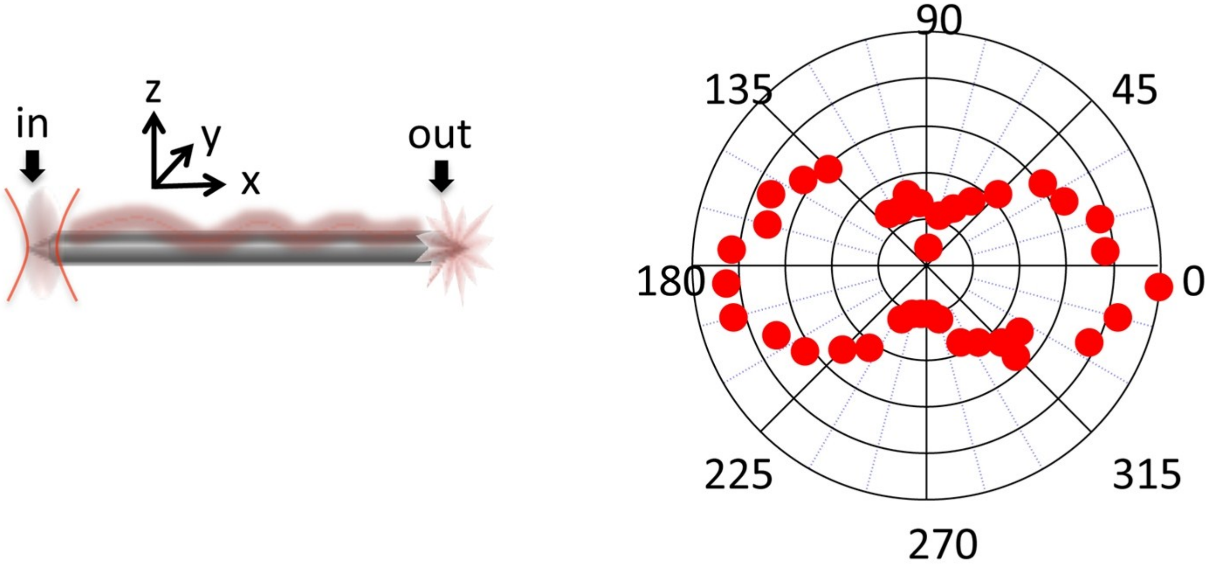


Figure S7 Polarization of remotely excited SHG emitted from the distal end of AgNW at the position indicated as ‘out’.

References:

S1. K. E. Korte, S. E. Skrabalak and Y. N. Xia, *J Mater Chem*, 2008, **18**, 437-441.