Supporting information of

Synthesis of Silver Nanoplates Based Two-Dimension Plasmonic Platform from 25 nm to 40 µm: Growth Mechanism and Optical Characteristic Investigation In-situ

Xiao-Yang Zhang^{a, b, c}, Huan-Li Zhou^{a, c}, Feng Shan^{a, c}, Xiao-Mei Xue^{b, c}, Dan Su^{b, c}, Yi-Ran Liu^a, Yu-Zhang, Chen

^{*a*}, Jing-Yuan Wu^{*a*, *c*} and Tong Zhang*^{*a*, *b*, *c*}

^a Joint International Research Laboratory of Information Display and Visualization, School of Electronic Science

and Engineering, Southeast University, Nanjing, 210096, People's Republic of China.

^b Key Laboratory of Micro-Inertial Instrument and Advanced Navigation Technology, Ministry of Education, and

School of Instrument Science and Engineering, Southeast University, Nanjing, 210096, People's Republic of

China.

^c Suzhou Key Laboratory of Metal Nano-Optoelectronic Technology, Suzhou Research Institute of Southeast

University, Suzhou, 215123, People's Republic of China.

Corresponding Author *Email: tzhang@seu.edu.cn

1. Discussion on the role of H_2O_2 in the seeds synthesis and the following nanoplate growth processes

The function of seeds synthesized with different amounts of H_2O_2 was compared. As the amount of AgNO₃ was the same in different seed solution, we distinguished the different seed solution samples by the molar ratio between H_2O_2 and AgNO₃. Identified from the extinction spectra of these seed solution shown in Figure S1a, there is not obvious differences in their size and morphology features when molar ratios of H_2O_2 : AgNO₃ increased from 0:1 to 50:1. When the molar ratios increased to 100:1, a wide LSPR band at about 600 nm was observed in the extinction spectrum. It indicated that silver nanoplates (SNPs) randomly generated and rapidly grew up in the seeds synthesis step once the amount of H_2O_2 added is too much.



Figure S1. (a) Extinction spectra of seed solutions synthesized with different amount of H_2O_2 . (b) Extinction spectra of SNP solution synthesized by employing different types of seeds. The amounts of seeds were 200 μ L for all four samples. Green circle illustrates the absorption band of nanospheres.

Next, we synthesized SNPs by Method 1 using these seeds obtained by different molar ratios of H_2O_2 : AgNO₃ and measured their extinction spectra show in Figure S1b. This comparison

experiment result shows the decisive role of H_2O_2 in the shape and yield control of SNP growth process clearly. When seeds synthesized without the addition of H_2O_2 were used for SNP synthesis, absorption band at 420 nm corresponding to LSPR of spherical by-products was clearly observed in the extinction spectrum (0:1). When seeds synthesized with molar ratios of H_2O_2 : AgNO₃ = 25:1 and 50:1, the absorption band at 420 nm was completely eliminated seen from their extinction spectra. However, when the ratio increased to 100:1, too much amount of H_2O_2 in the seed solution broke the reaction balance of the SNP growth step and influenced the uniformity of SNPs. Therefore, the optimal range of molar ratio between H_2O_2 and AgNO₃ for monodispersed SNP synthesis is between 25:1 and 50:1.

Figure S2 shows SEM images of 100% yield SNP Type I. The morphology of the SNP are in high uniformity, established the advantage of current proposed seed screening method. There is not any spherical particle at all seen from the large-scale area of the SEM. Insets show the thickness and the particle size of these SNPs.





Figure S2. SEM images of SNP Type I with small size. Insets show the thickness (upper) and the size of the SNP.

Figure S3. Comparison of extinction spectra of SNP samples synthesized using different type of seeds. P1 represents SNP samples synthesized using conventional seeds with polydispersed crystalline type where H_2O_2 is 0. P2 represents the SNP Type I with 100% yield SNPs synthesized using seeds obtained under optimal condition (H_2O_2 : AgNO₃ = 50:1). Insets show the solution and SEM images of these two samples.

The color of SNP solutions is also highly dependent on the purity of the SNPs. Figure S3 compared two samples with a similar main LSPR band at ~ 760-770 nm synthesized using different types of seeds. The only difference between the two samples is that there were a small quantity of by-product existed in sample P1. It can be seen clearly that green color is observed once silver spheres existed, as seen from the photograph image. SEM image of sample P1 indicated that there were a lot of silver spheres in the solution. The band at 420 nm (highlighted by a green circle) seen

from the extinction spectrum in Figure S3 corresponds to the main LSPR band of these by-product of silver spheres. This sub-band is absent seen from the extinction spectrum of Sample P2. Once 100% yield of SNPs solution (Sample P2) with a similar main LSPR band (at about 760-770 nm) was obtained, the color of the solution became blue as shown from the photograph image. Therefore, there is a rapid and direct way to identify the purity of the synthesized SNP solution by directly monitoring the color change phenomenon during the synthesis process. Once the green color was absent, it means that spherical by-products had been fully avoided.

This H_2O_2 assisted synthesis method is very robust because the amount of monodispersed SNP synthesized in one single growth can be enlarged to 0.32 g (0.012 M). Photographs in Figure S4 show the original and diluted (to ~1‰) SNP solutions synthesized. To the best of our knowledge, it is the highest density of SNPs solution synthesized in aqueous environment, over100-fold larger than that of previous reports.



Figure S4. Photographs of as-prepared SNPs Type I solution and diluted one (inset).

2. Crystal structure characterization of SNPs



Figure S5. (a) TEM image of the edge of SPN type II. The yellow circle marked the position where HRTEM in (b) and selected area electron diffraction pattern in (c) were measured.

Figure S5a shows typical morphology of SNP type II having defects. A nano-groove with a size of less than 10 nm was clearly observed at the edge of SNP. HRTEM image and selected area electron diffraction (SAED) pattern in Figures S5b and S5c were taken from the positon illustrated by yellow circle. The results exhibited the single-crystalline structural characteristic of SNPs. Figures S6 shows the thickness of SNP Type III.



Figure S6. SEM images reflecting the thickness of typical SPNs type III.

Figure S7 shows a giant SNP Type III with a size of 40 μ m. To the best of our knowledge, this is the highest aspect ratio of ultrathin SNP achieved by chemical synthesis method.



Figure S7. Optical image of SPN type III with an ultra-large size. The sample was prepared without centrifugation.

The compared XPS spectra between SPN type II and SPN type III in full spectrum range is shown in Figure S8.



Figure S8. Comparison of XPS analysis between SPN type II and SPN type III in full spectrum range.





Figure S9. Numerical simulation results of mode intensity distribution of two-dimensional infinite SNP waveguides with different thicknesses and dielectric environments taken from the cross-sections view. (a) to (c) show the asymmetric cases where n₁ = 1.52 and n₂ = 1.0 at excitation wavelengths of 473 nm, 532 nm and 785 nm, respectively.
(e) to (g) show the symmetric case where n₁ = n₂ = 1.52 at excitation wavelengths of 473 nm, 532 nm and 785 nm, respectively. Dashed lines illustrate the position at 1/e² of the normalized intensity. The thickness dependent mode widths W for asymmetric and symmetric cases are shown in (d) and (h), respectively.

Thickness dependent mode intensity distributions at the center of the 2D planar SPP waveguides with asymmetric and symmetric configurations are shown in Figures S9a-c and S9e-g, respectively.

Relationships between *W* and thickness *T* of the SNPs for asymmetric and symmetric configurations are shown in Figures S9d and h, respectively. Here the mode width *W* corresponds to the cross-section distance where the intensity decreases to $1/e^2$ of normalized intensity.

For asymmetric waveguide configurations, the mode volumes do not change obviously with the decrease of *T* at wavelengths of 473 nm and 532 nm. It represents that the light confinement of these thinner SNPs is still excellent although the thickness decreases. For symmetric waveguide configurations, the mode volumes change obviously and the mode widths *W* increase when *T* is as thin as 15 nm at all three wavelengths. As more power of mode extends to dielectric layer with low losses, the propagation length of SPP mode is greatly prolonged, accordingly. This simulation result indicates that the successful synthesis of ultrathin SNP is important progress for the realization of long-range SPP waveguides with low optical losses.

To explain the relationship between the mode propagation loss and the thickness *T*, we further investigated the mode power ratio distributed at different region of the waveguide at different excitation wavelengths, as shown in Figure S10. The mode propagation losses increase when more power of the modes distributed inside silver. It is clearly observed, when thickness of the SNPs is thicker than 100 nm, the power ratios of these waveguides at different excitation wavelength are almost the same. It is because such thick SNPs support pure boundary modes independent on the thickness. When the thickness decreased gradually, the power ratio in dielectrics increased accordingly, especially for the symmetric case.



Figure S10. (a) Calculated power ratio in silver and dielectric of two-dimensional infinite SNPs samples with different excitation wavelength. The SNP was immersed in dielectrics ($n_1 = n_2 = 1.52$) and exacted by light with $\lambda = 473$ nm, 532 nm and 785 nm, respectively. (b) Calculated power radio in silver and glass substrate of two-dimensional infinite SNPs samples with different excitation wavelength. The SNP was placed on the surface of a glass substrate ($n_1 = 1.52$) and covered by air ($n_2 = 1.0$), and the exaction wavelength were 473 nm, 532 nm and 785 nm, respectively.

4. Scheme of the experiment setup for the SNP in-situ excitation and spectral measurement



Figure S11. Schematic illustration of experiment setup for SNP excitation and optical spectral measurement *in-situ*.

The measurement and in-situ imaging was based on Olympus IX-71 optical microscope, as illustrated in Figure S11. A 50 / 50 BSP was used to control the excitation direction of the focused laser beam. When the BSP is rotated, the incident angle of the focused laser beam becomes oblique

accordingly, and the excitation efficiency of the SPP modes decreases in according to the rotation angle of the BSP.



5. Optimization condition discussion of the imaging resolution

Figure S12. (a) and (b) show excitation of SPP modes using SNP type III with different $\delta\theta$ excited by 473 nm laser. (c) and (d) show the normalized scattering spectra at different positions where illustrated by white circles in (a) and (b)

As discussed above, the excitation angle and direction of the SPP modes can be influenced by rotating the angle of BSP. Therefore, the spatial distribution of the scattered light at the output port of the SNP waveguides can be changed by rotating BSP. It leads to an improvement of imaging resolution of the scattering signals on the 2D plasmonic platform. Scattering spectra taken from different positions at different rotation angles of BSP were compared as shown in Figure S12. When $\delta\theta$ changed from 0° to 10°, the measured scattering intensities at positions 2 and 3 decreased obviously. It led to an improved spatial resolution as well as suppressed signal-to-noise ratio when the platforms are used for subwavelength imaging and sensing.

6. Excitation of 2D SPP mode propagating along SNP type III waveguides at different wavelengths.



Figure S13. (a) Optical images of 2D SPP mode propagation excited by different wavelengths. (b) Measured scattering light intensities at output edges of SNPs as a function of $\delta\theta$

Figure S13 shows that SPP modes with wavelength from visible to infrared range can be effectively excited and remotely manipulated on the 2D SNP based plasmonic platform. The intensities of the edge scattering signals can be tuned effectively by rotating the angle of BSP.

7. Multiple wavelengths transmission of SNPs

Figure S14a shows the scattered images of linear source excited by supercontinuum laser. The excitation wavelengths, from left to right, are 530 nm, 570 nm and 600 nm, respectively. Three laser beams were focused on one edge of the SNP simultaneously. Scattering spectra were taken from another edge indicated by the red arrow, as show in Figure S12b. Apparently, the magnitudes of the scattering intensities at different wavelengths can be tuned simultaneously by rotating BSP,

from the state of 'on' to 'off'. The relationship between the peak intensity of the three wavelengths and $\delta\theta$ was recorded in Figure S14c.

Similar experiment was also demonstrated using SNP type II, as shown in Figure S14d-f. The hot spot far away from the excitation edge effectively served as a nanoantenna to scattering multiple wavelength signals at a subwavelength volume. The scattering intensities of the SPP modes with three different wavelengths can also been tuned simultaneously by BSP rotation. The results exhibited the excellent broadband light manipulation ability of SNP platforms.

Here we further explored the efficiency of the current focusing excitation method. Dashed line in Figure S14e recorded the scattering spectrum of the focused laser beams *in-situ*. In comparison, when the focused light partially coupled into SPP modes, propagated along the SNP waveguide for several micrometers and finally scattered into free-space at the scattering port, most part of light energy dissipated. Therefore, the intensity of the scattering light received from the scattering port in far-field becomes much weaker. We compared the ratio between the magnitudes of intensity of the focused laser beams *in-situ* I_{substrate} and the scattering intensity I_{hot spot}. The results indicated that I_{hot} spot / I_{substrate} = 1.723%, 0.988%, and 1.008% for the incident wavelength of 530 nm, 570 nm and 600 nm, respectively. These values are relative low owing to both the low excitation efficiency of the laser focusing method and the high propagation loss nature of SPP modes. Therefore, we believe further studies focusing on the excitation efficiency improvement of SPP modes from free-space light are of great importance.



Figure S14. Excitation of SNP type III using single wavelength of 530 nm, 570 nm and 600 nm, or their mixture. (b)
Light scattering spectra taken from output port illustrated by red arrow in (a). (c) Light intensity variation as a function of rotation angle (θ). Analogous images and plots SNP type II are shown in (d)-(f). The dashed line in (e) represents the scattering spectrum taken from a focused laser spot vertically reflected from a glass substrate without SNP.

8. Captions for Supplemental Movies

Supplementary Movie 1. Reaction procedure of the seeds synthesis process showing the robustness of self-screening behavior of H_2O_2 was recorded.

Supplementary Movie 2. Camparison of the etching phenomena of H^+ during the crystal growth reaction by *in-situ* monitoring a single SNP with or without the protection of Cl⁻ recorded under the

optical microscope observation. The reaction process was directly recorded by the CCD camera under $100 \times$ objective lens. In this comparison experiment, regrowth solutions with or without the addition of Cl⁻ were dropped on the surface of glass substrate under the observation of optical microscope. The movie recorded the reaction procedures after a drop of AgNO₃ was added. Without the protection of Cl⁻, the SNP gradually dissolved once H⁺ generated from the reaction described by Equation 1. In comparison, when certain amount of Cl⁻ was added, the SNP become stable even when H⁺ gradually accumulated with the same reaction procedure. However, this SNP did not grow up obviously either. We believe it may because the reaction condition of SNP regrowth process such as high speed stirring is absent under optical microscope observation. The reduced Ag atoms cannot be absorbed on the lateral surfaces of SNPs with such a large size in-time, blocking the size increase of SNP.