Electronic Supplementary Information

Seed-Mediated Growth of High Yield Au Nanoplates with In-situ Generated Au Clusters through Galvanic Replacement

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1. Experimental Section

Materials.

Hydrogen Tetrachloroaurate (III) Trihydrate ($HAuCl_4 \cdot 3H_2O$), Polyvinylpyrrolidone K30 (PVP), (-)-Glutathione oxidized (98%), Sodium Citrate (TSC, 98%+) and Sodium Borohydride ($NaBH_4$, 98%) were purchased from Adamas Reagent Co., Ltd. Sodium Hydroxide (NaOH) was purchased from General-Reagent Co., Ltd. Silver nitrate ($AgNO_3$), tetrahydrofuran (THF, $\geqslant$ 99.5%), glycerol (99%) and Methanol ($\geqslant$ 99.8%) were purchased from Sinopharm Chemical Reagent Co., Ltd. The deionized water (18.2 MΩ cm) used in the experiments was provided by a Sartorius arium basic water-purification system (Gottingen, Germany). All chemicals were used as received without further purification.

Method

Synthesis of 4 nm Ag nanoparticles (Seeds)

Silver nanoparticles were synthesized according to the procedure reported. Typically, 95 mL of H_2O, 0.5 mL of 30 mM $AgNO_3$ and 1 mL of 1% (w/v) TSC were combined in a 150 mL beaker before bubbled with nitrogen gas for 30 min. Then, the beaker was immersed in an ice bath for 30min under vigorous. 1 mL of 50 mM $NaBH_4$ (freshly prepared with ice-cold water) was rapidly injected into the solution. Over the next 20 min, five drops of the $NaBH_4$ solution were added into the beaker every 2 min to ensure that the reaction is slow and uniform enough. After that, 0.5 mL of the $NaBH_4$ solution and 0.5 mL of 5 mg/mL PVP were added dropwise into the mixture. The resulting solution of Ag nanoparticles was gently stirred for 3 h in the ice bath and allowed to be kept at about 4 ℃ in dark before use.

Synthesis of Ag nanoplates

The Ag nanoplates were prepared with a photocatalytic reaction to reduce the A (III) precursor. First, 4.5 mL of H_2O, 0.5 mL of 5 mg/ml PVP, 0.5 mL of CH_3OH and 0.16 mL of 1% $HAuCl_4$ were combined in a 10 mL glass bottle respectively. The mixed solution was made up to 6 mL and gently mixed to serve as the growth solution. Then, 5 μL of Ag seed was added to this growth solution. The glass bottle filled with solution was illuminated for about 6 h with a Xenon lamp (Perfectlight, PLS-SXE300 $\pm$ 20) equipped with a band-pass filter (Perfectlight, PLS-BP20500) from the side. All the growth experiments were performed under the incident power of 15 W and the incident wavelength of λ=520 $\pm$ 20 nm unless otherwise specified. The solution gradually changed from light yellow to brick red, indicating that Au nanoplates were formed. The products were collected by centrifugation at 2500 r.p.m. for 5 min and washed twice with deionized water to remove the excess surfactant. Finally, the samples were re-dispersed in 2 mL of deionized water for subsequent characterization.

Synthesis of 30 nm Ag nanoparticles

30 mL of H_2O and 20 mL of glycerol were mixed in a 100 mL flask at 95℃. Then, 9 mg of $AgNO_3$ was added into the solution under vigorous, followed by 1 mL (3%) of TSC after 1 min. The solution was kept at 95℃ for 1 h. Finally, the as-synthesized Ag nanoparticles were centrifuged and stored at 4℃ before used.

Synthesis of Au nanoclusters

1.6 mmol of $HAuCl_4 \cdot 3H_2O$ was added into 44 mL of THF in a tri-neck flask and kept in an ice bath for 30 min. Then, 8 mmol of glutathione was slowly added to the solution under slow stirring. The color of the solution turned colorless after 24 h, followed by the quick addition of 15 mL of 1.25 M fresh $NaBH_4$ under fast stirring. The reaction was kept at constant stirring for 3 h. After that, the solution was heated to 45℃ for further proceed of 2 h. The supernatant was kept at 4℃ before used.

Characterization

The morphologies and structures of the samples were characterized by transmission electron microscopy (TEM, JEM-F200), field emission scanning electron microscope (SEM, ZEISS SIGMA) and atomic force microscope (AFM, PARK NX10). Crystal structures of the Au nanoplates were identified by X-ray powder diffractometer (XRD, SMARTLAB SE) with Cu Kα irradiation λ = 1.54 Å) at 40 KV, 30 mA, and a scan rate of 2 °/min. The UV-vis absorption spectra of the samples were collected using UV-vis-NIR spectrophotometer (CARY5000) in the range of 400-1500 nm. The SHG single was characterized by Spectroscope (ACTON SP 2300I) under a laser of 2.6 mW, 20 MHz and 1300 nm. Matrix-assisted laser desorption/ionization time of flight (MALDI-TOF, AUTOFLEX MAX) was operated in the negative ion mode. The percentage of Ag and Au was characterized by inductively coupled plasma mass spectrometry (ICP-MS, PQ-MS). Electrospray ionization mass spectrum (ORBITRAN FLITE) was used to characterize the seeds after the galvanic exchange.
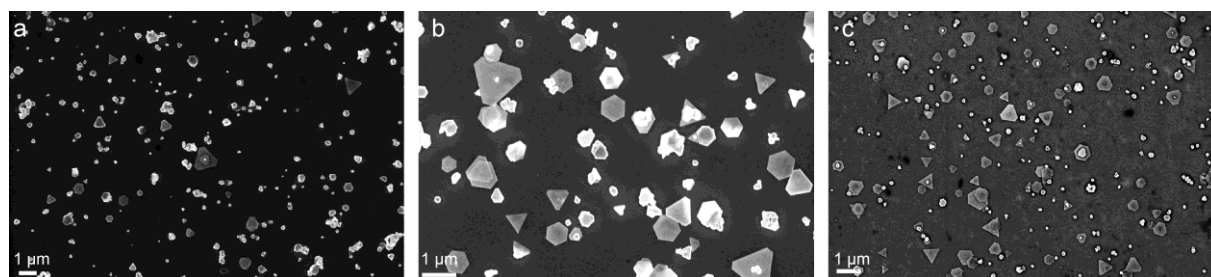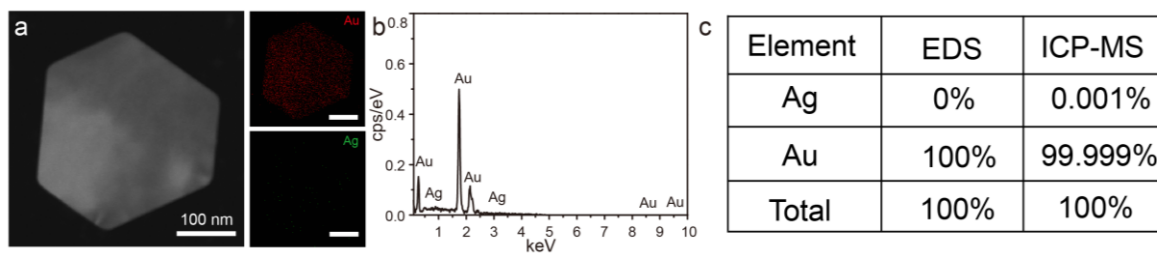
2. Supplementary results
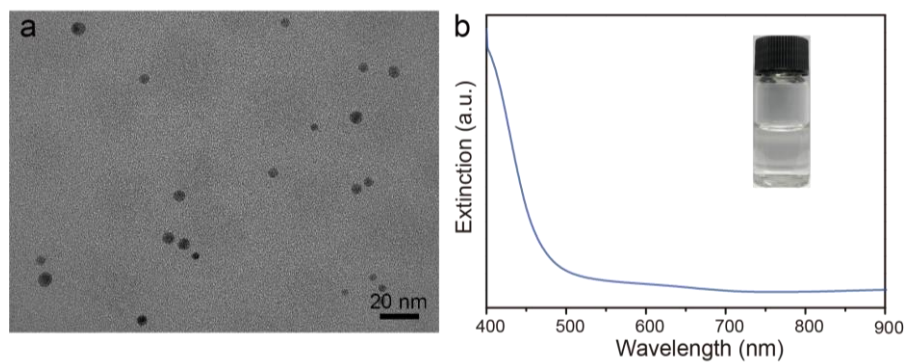
Fig. S1 (a) TEM image of Ag seeds. (b) UV-vis spectrum of the solution before reaction.
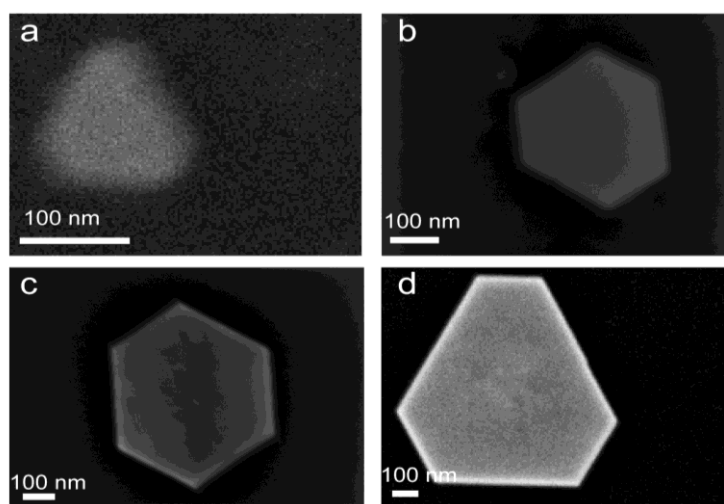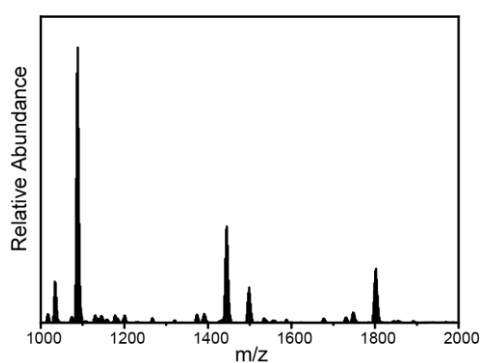

Fig. S2 SEM images of the intermediate specimens taken over the course of reaction from (a) 10 min, (b) 30 min, (c) 1 h, (d) 2 h.
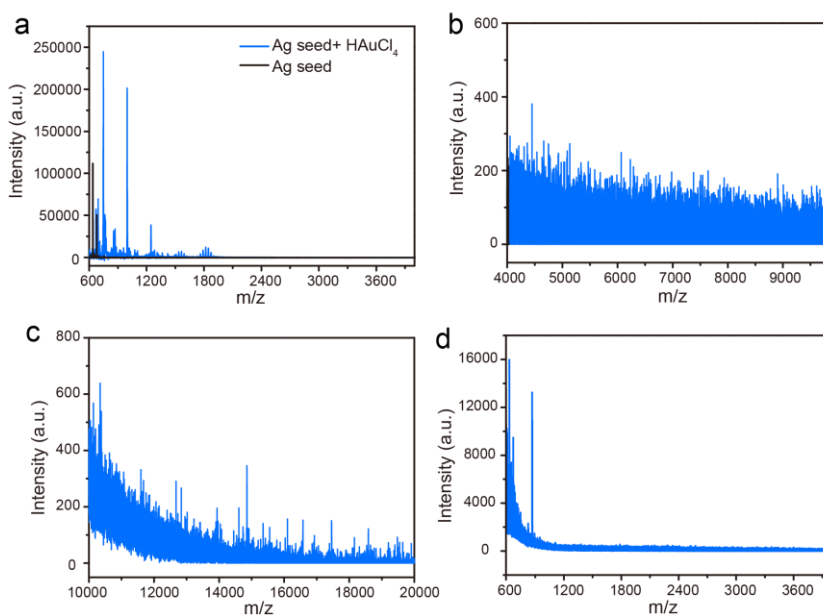

Fig. S3 SEM images of Au nanoplates made by different incident wavelength. (a) 400 nm, (b) 600 nm, (c) 700 nm.

Fig. S4 (a and b) EDS of the Au nanoplates. (c) The concentration of Au and Ag measured by EDS and ICP-MS.


Fig. S5 Electrospray ionization MS spectrometry of Ag seeds after galvanic exchange of 1000-2000 m/z.


Fig. S6 (a) MALDI-TOF spectrometry of Ag seeds before and after galvanic exchange of 600-4000 m/z. (b and c) MALDI-TOF spectrometry of Ag seeds after galvanic exchange of 4000-20000 m/z. (d) MALDI-TOF spectrometry of 30 nm Ag nanoparticles after galvanic exchange of 600-4000 m/z.
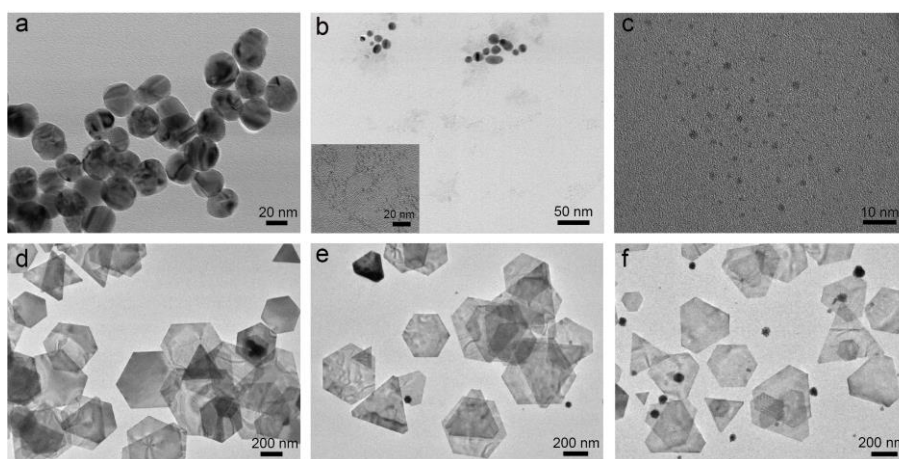
Fig. S7 (a) TEM image of 30 nm Ag nanoparticles. (b) TEM image of 30 nm Ag nanoparticles after galvanic exchange. (c) TEM image of Ag seeds after galvanic exchange. (d-f) TEM images of Au nanoplates made by 2 μL, 5 μL and 20 μL Ag seeds.
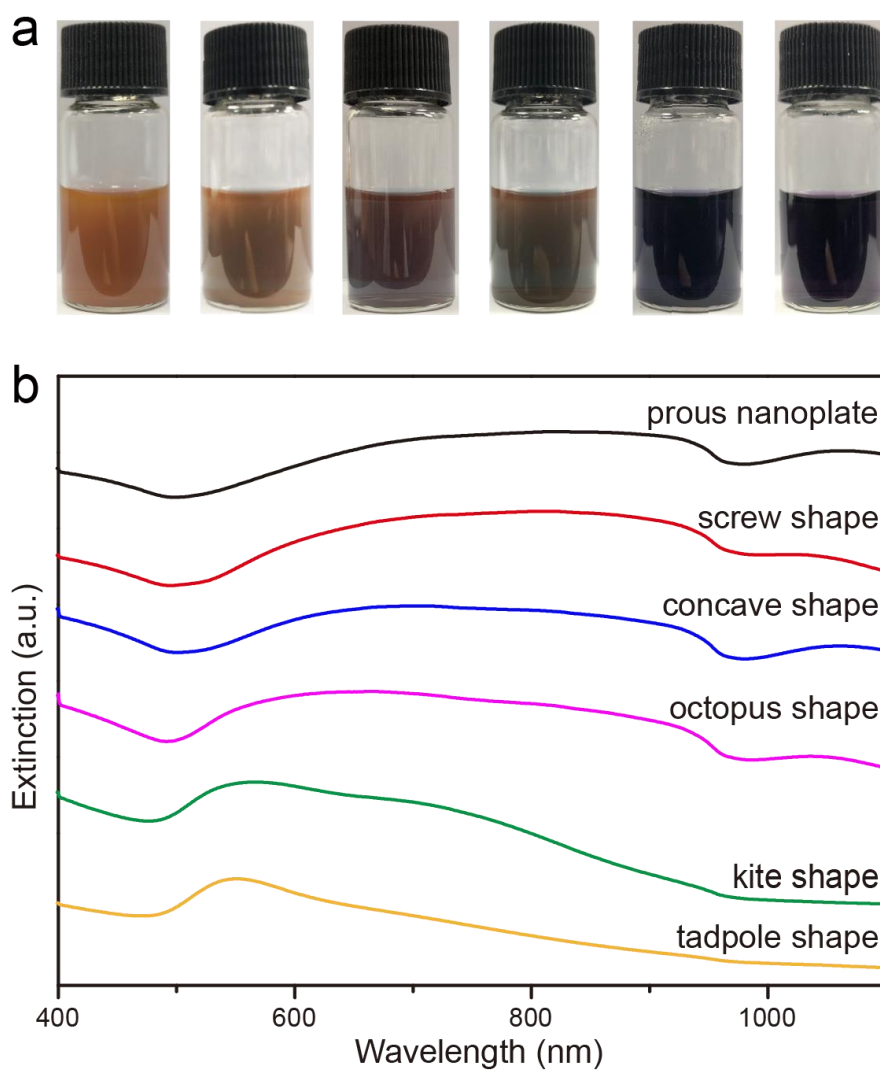

Fig. S8 (a) Photos of the solution made by addition of different amount of NaOH. From left to right: 880 μL, 920 μL, 960 μL, 1150 μL, 1250 μL and 1400 μL. (b) UV-vis spectrum of different shapes of Au nanoplates.
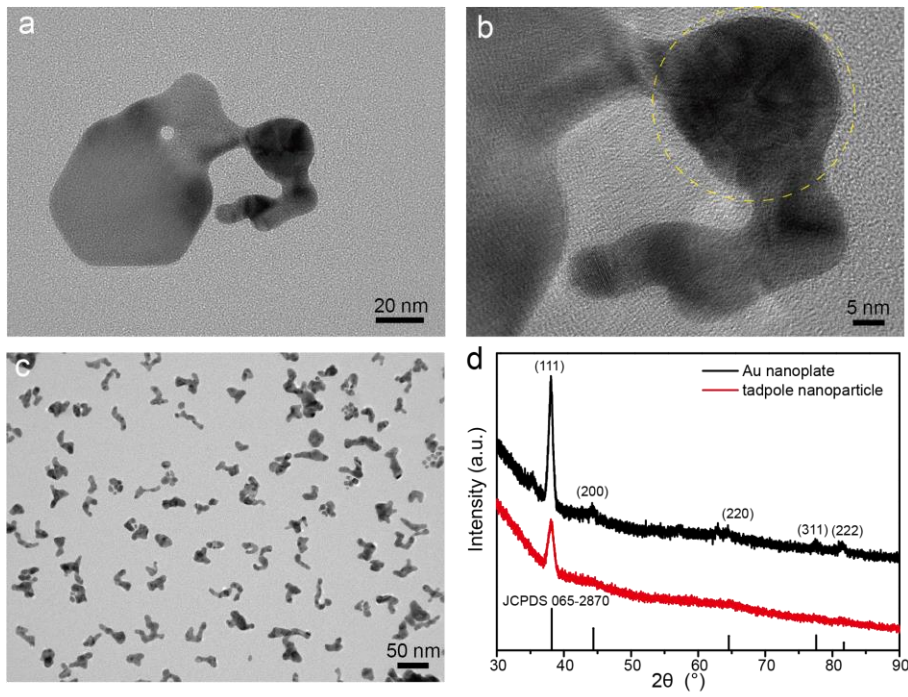
Fig. S9 (a and b) TEM images of the tail-shaped nanoplates. (c) TEM image of products after NaOH is excessive. (d) XRD of the initial nanoplates and the tail-shaped nanoplates.
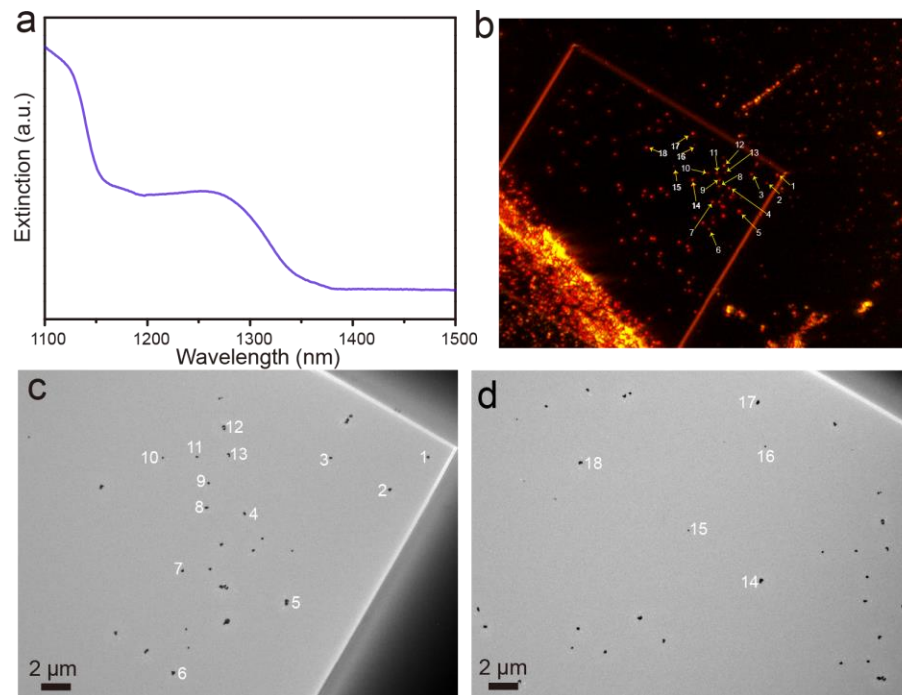
Fig. S10 (a) Absorption spectrum of nanoplates within 1100-1500 nm. b) dark-field micrographs of the nanoplates on SiN$_x$. (c and d) TEM images of the Au nanoplates on SiN$_x$.
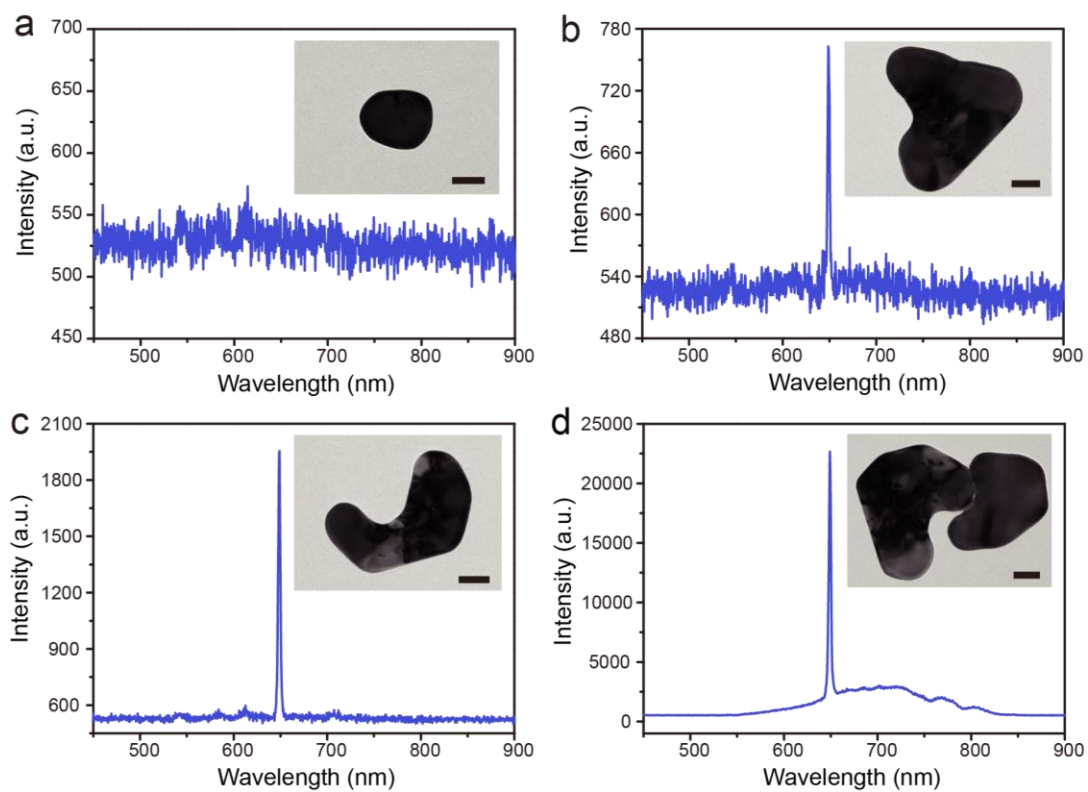
Fig. S11 TEM images of several different shapes of Au nanoplates along with their SHG signals. All scale bars represent 50 nm.