# Highly Stable Ag@Au Nanoplates and Nanoframes for Two-Photon Luminescence

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## Experimental Section

*Synthesis of Ag TNPs.*

Pure Ag TNPs with 730 nm in-plane dipole plasmon resonance were synthesized following reported procedure.[1] The reaction was carried out in dark and at room temperature. 3 mL TSC (30 mM), 3 mL PVP (Mw≈58000 g/mol, 0.7 mM) and 120 μL $H_2O_2$ (30 wt.%) were added into $AgNO_3$ (0.1 mM 50 mL) solution with violently stirring. 5 min later, 0.6 mL fresh $NaBH_4$ (100 mM) was added rapidly, along with the solution changed from colorless to pale yellow. 30 min later, the color was changed quickly from yellow to red, purple, and finally maintained at blue. The whole transformation process was in less than 2 min. After centrifuging at 10000 rpm for 20 min, bottom Ag TNPs were dispersed in 55 mL deionized water and got 5 mL for subsequent characterization. Pure Ag TNPs with 798 nm in-plane dipole plasmon

resonance was prepared as the same procedure but the fresh $NaBH_4$ was changed to 0.45 mL.

*Synthesis of Ag/Au TNF samples.*

$HAuCl_4$ (1 mM) was injected into the 730 nm in-plane dipole plasmon resonance Ag TNP solution with the speed as 10 μL/min via a peristaltic pump. Ag/Au TNF samples containing different quantity of $HAuCl_4$ was prepared by sampling at corresponding injection time. 5 mL Ag/Au TNF sample containing 1 ppm $HAuCl_4$ was obtained after injecting 5 min, then 5 mL Ag/Au TNF sample containing 2-ppm $HAuCl_4$ was obtained after further injecting 4.5 min, then 5 mL Ag/Au TNF sample containing 3 ppm $HAuCl_4$ was obtained after further injecting 4 min. Similarly, the last 5 mL Ag/Au TNF sample containing 10 ppm $HAuCl_4$ was obtained after injecting 0.5 min.

*Characterization.*

TEM was performed on transmission electron microscopes (Hitachi T-7700) for characterizing the shapes and structures of all the nanocrystals. Absorption spectra of the nanocrystals (suspended in water) were recorded using a UV–Vis spectrophotometer (Unico 2802PC). The elemental analysis was investigated by inductively coupled plasma atomic emission spectrometer (ICP-7500). The TPL emission spectra measurements were characterized using a regenerative amplifier (Spitfire, Spectra Physics) seeded with a mode-locked Ti:sapphire laser (Tsunami, Spectra Physics) generated laser pulses of about 120 fs at a wavelength of 795 nm, which were used to drive an optical parameter amplifier (OPA-800CF, Spectra Physics) to obtain a tunable laser in the range of ca. 550-750 nm. The laser beam was focused into a quartz cuvette having an optical path length of 10 mm. The two-

photon-induced fluorescence was collected with a right angle geometry and detected with a liquid-nitrogen-cooled charge coupled device (CCD) detector (SPEC-10-400B/LbN, Roper Scientific) attached to a polychromator (Spectropro-550i, Acton). The intensity of TPL emission was addressed with Rhodamine B as a reference. A 750 nm short pass filter was placed before the spectrometer to minimize the scattering from the excitation light.

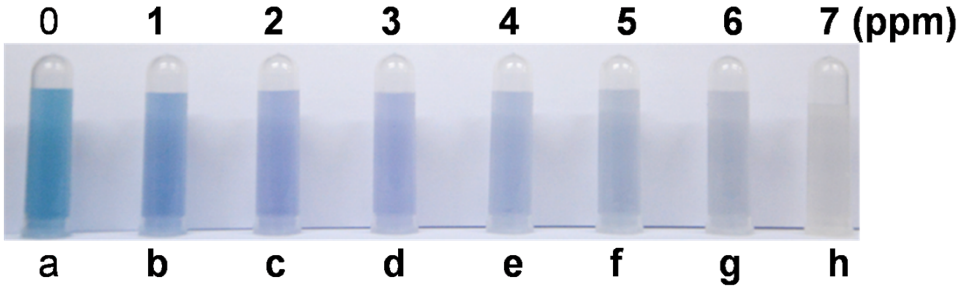


**Figure S1.** Digital images of Ag TNP solution and its Au/Ag TNF derivatives formed by introducing $HAuCl_4$ with a final concentration of 1 to 7 ppm (corresponding a~h, respectively).

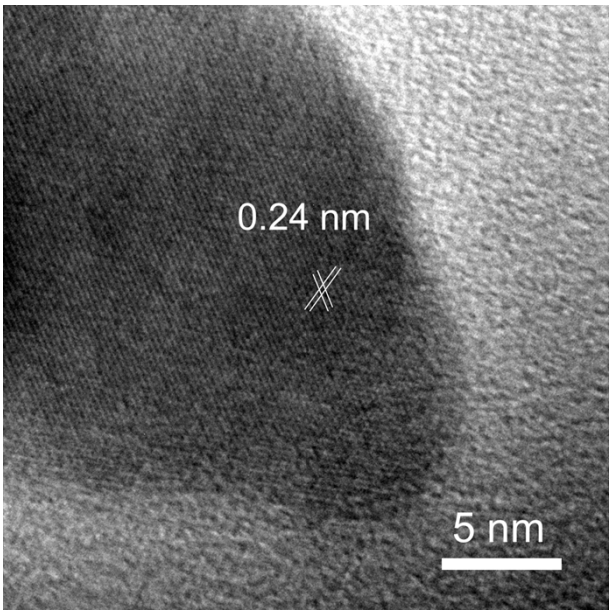


**Figure S2.** High-resolution TEM image of basal face of 1 ppm $HAuCl_4$-containing-Ag/Au TNP, with main [111] face and different crystal domain near the crooked edge.

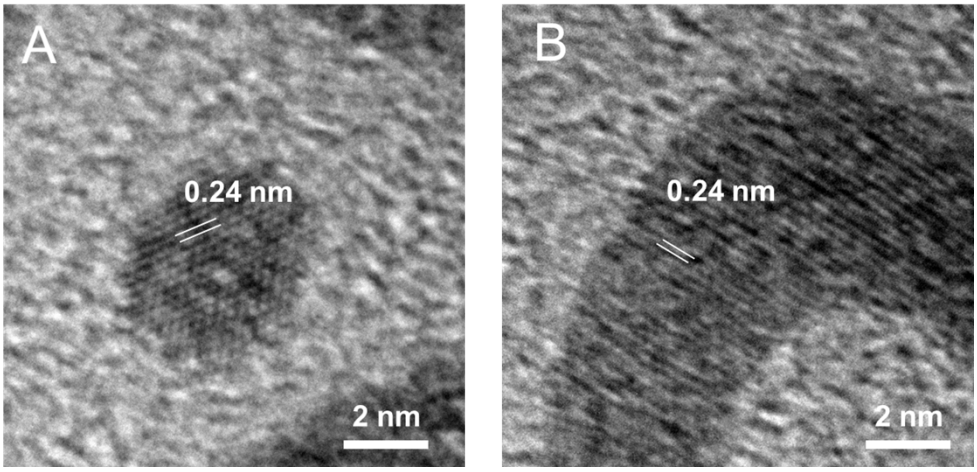


**Figure S3.** High-resolution TEM image of leftover part and remained frame of 5 ppm $HAuCl_4$-containing-Ag/Au TNF, with main [111] face.

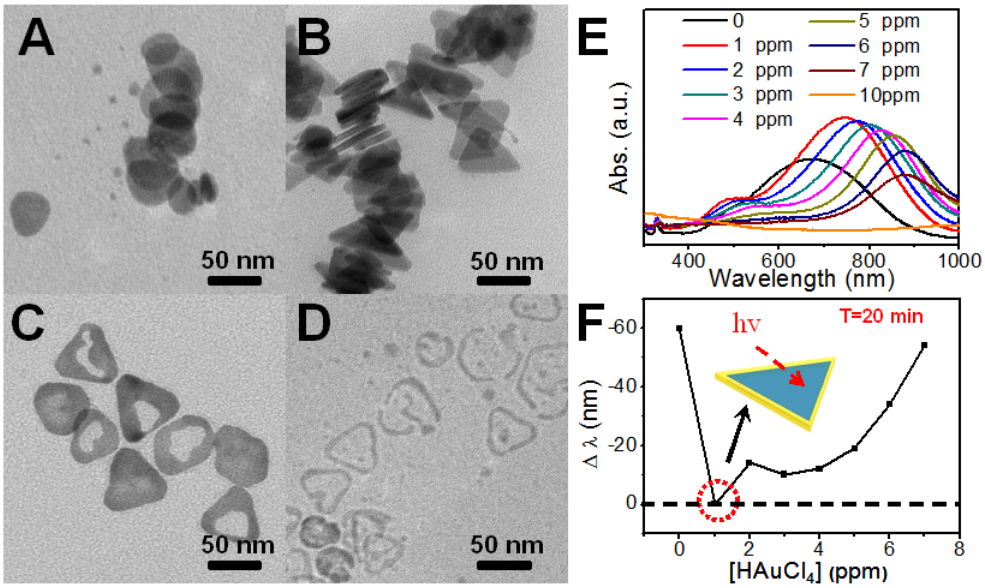


**Figure S4.** (A, B, C, D) TEM images and (E) UV-Vis spectra of Ag TNPs and 1, 4, 7 ppm $HAuCl_4$-prepared Ag/Au TNFs after NIR irradiation. (F) Plots of the blue-shifted wavelength of the main LSPR versus the corresponding samples after irradiation.

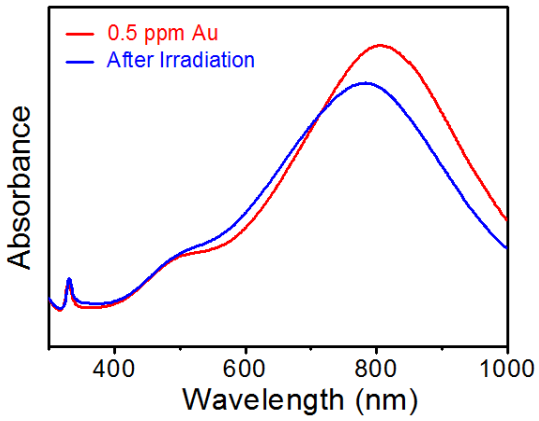


**Figure S5.** UV-Vis spectra of Ag/Au TNPs prepared with 0.5 ppm $HAuCl_4$ before and after irradiation.

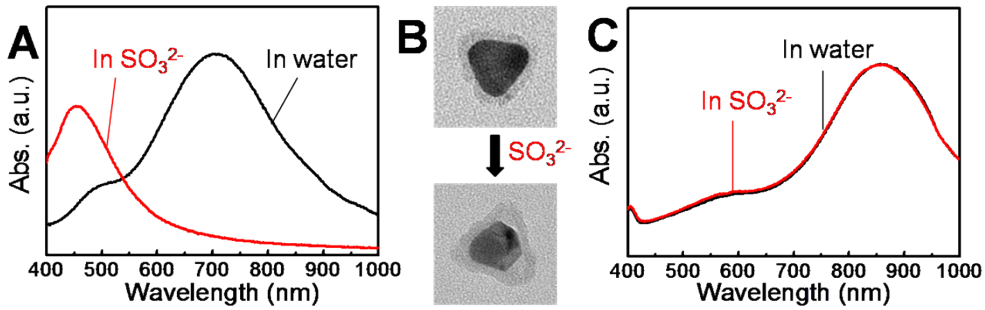


**Figure S6.** (A) UV-Vis spectra of Ag TNP@$SiO_2$ in deionized water and in $SO_3^{2-}$ solution (0.1 M) after 10min. (B) Corresponding TEM images of Ag TNP@$SiO_2$ before and after meeting $SO_3^{2-}$. (C) UV-Vis spectra of Ag/Au TNFs in deionized water and in $SO_3^{2-}$ solution (0.1 M) after 7 days.

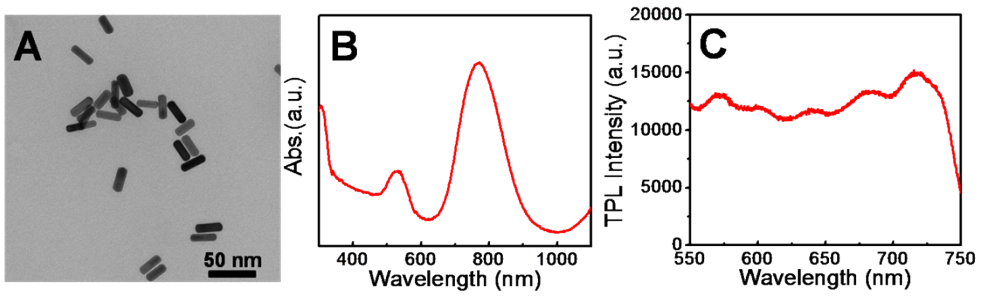


**Figure S7.** (A) TEM image, (B) UV-Vis and (C) TPL spectra of Au NRs in deionized water.

**Calculation of Two-photon action cross section:**

Concentrations of Au NR reference ($C_{AuNR}$) and Ag TNP sample ($C_{AgTNP}$) were calculated from ICP elemental analysis (by using equation 1) and their average sizes which were obtained from TEM images (Fig. S4A and Fig.1A) (by using equation 2 and 3):

$$C_{NS} = \frac{C_m}{\rho V} \qquad (1),$$

where $C_{NS}$ represents the concentration of nanostructures, $C_m$, ρ and V are the concentration of elemental analysis, the density of metal and the volume of single particle, respectively. ($\rho_{Au}$=19.3 g·cm$^{-3}$, $\rho_{Ag}$=10.5 g·cm$^{-3}$).

$$V_{AuNR} = \frac{4}{3}\pi R^3 + \pi R^2 (l - 2R) \qquad (2),$$

where R and l are the radium and the length of single Au NR, respectively.

$$V_{AgTNP} = \frac{\sqrt{3}}{2} l^2 h \qquad (3),$$

where l and h are the side length and the height of single Ag TNP, respectively.

According to calculations, the concentration of Au NR and Ag TNP are 2.3pM and 0.51pM.

The two-photon action cross section of coupled metal nanoparticles was calculated according to equation (4):

$$\varphi_{2p(sample)} = \varphi_{2p(ref)} \frac{I_{sample} C_{ref} n_{sample}^2 P_{ref}^2}{I_{ref} C_{sample} n_{ref}^2 P_{sample}^2} \qquad (4),$$

where $\varphi_{2p}$ is the two-photon action cross section, I is the integrated TPL intensity obtained from TPL spectra Fig. S1C and Fig.2A), C is the concentration calculated above, n is the refractive index and P is the incident power which are same for Ag TNP sample and the Au NRs reference. The two-photon action cross section of Au NRs is $\varphi_{2p\ (ref)}$=30 000 GM (at 820nm, 1 GM=$10^{-50}$cm$^4$·s/photon), according to Han. F and Zijlstra, P. *et al*.[2,3]

The integrated TPL intensity of Ag TNPs ($I_{sample}$) and AuNRs ($I_{ref}$) are 1777784 and 2448644, respectively. According to equation 4, the two-photon action cross section of single Ag TNP is calculated to be 98300 GM. The integrated TPL intensity of Ag/Au TNF samples containing $HAuCl_4$ of 1, 3, 5, 7 ppm are obtained from Fig. 2A as 1147794, 795725, 589604, 426464, respectively. Since the concentration of Ag TNP and its Ag/Au TNF derivatives are the same, the corresponding two-photon action cross section of single Ag/Au TNPs are 63466, 43998, 32601, 23581 GM, respectively.

**Reference:**


1. G. S. Métraux and C. A. Mirkin, *Adv. Mater.*, 2005, **17**, 412-415.
2. F. Han, Z. Guan, T. S. Tan and Q. H. Xu, *ACS Appl. Mater. Interfaces*, 2012, **4**, 4746-4751.
3. P. Zijlstra, J. W. Chon and M. Gu, *Nature*, 2009, **459**, 410-413.