

Supporting Information

for

Halide-assisted activation of atomic hydrogen for photoreduction on two-liquid interfacial plasmonic arrays

Yue Xu, Fanfan Yu, Mengke Su, Shanshan Du, and Honglin Liu*

College of Food and Biological Engineering, Engineering Research Center of Bio-process,
Ministry of Education, Hefei University of Technology, Hefei, Anhui 230009, China

Correspondence: liuhonglin@mail.ustc.edu.cn

Experimental Section

Chemicals and Reagents.

Chloroauric acid ($\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$, 99.9%), Hydroxylamine hydrochloride ($\text{NH}_2\text{OH} \cdot \text{HCl}$, 98.5%) were supplied from Nanjing Chemical Reagent Co., Ltd. Ethanol ($\text{C}_2\text{H}_6\text{O}$, 99.7%), glycerol ($\text{C}_3\text{H}_8\text{O}_3$, 99.9%) were purchased from Shanghai Titan Scientific Co., Ltd. PVP [$(\text{C}_6\text{H}_9\text{NO})_n$, 99.9%] was purchased from Sigma-Aldrich. Trisodium citrate ($\text{C}_6\text{H}_5\text{Na}_3\text{O}_7 \cdot 2\text{H}_2\text{O}$, 99%), Ag nitrate (AgNO_3 , 99.8%), Sodium chloride (NaCl , 99.5%), Potassium bromide (KBr , 98.5%), potassium iodide (KI , 98.5%), hydrochloric acid (HCl , 36-38%), sulfuric acid (H_2SO_4 , 98%), p-nitrothiophenol (4-NTP, 99.9%) were all bought from Sinopharm Chemical Reagent Co., Ltd. All chemicals were analytical reagent and used without further purification. Ultrapure water ($18.2 \text{ M}\Omega \cdot \text{cm}$) was produced using Millipore water purification system.

Apparatus

The morphology, structure and properties of as prepared AuNP and AgNW sol were characterized by Shimadzu UV-2600 spectrometer, JEOL 2010 high-resolution TEM. The scanning electron microscopy (SEM) images were taken by an Auriga focused ion-beam scanning electron microscopy (FIB-SEM). Raman spectra were performed on B&W Tek portable Raman spectrometer at 785 nm laser excitation. The laser focal spot on the metal surface was about 100 μm in diameter with a measured power of 90 mW. The etching of single AgNW was performed on a Lab-RAM HR800 spectrometer with

a 633 nm laser excitation source and recorded with a 20 min accumulation time. The laser focal spot on the metal surface was about 1 μm in diameter with a measured power of 2-3 mW.

Synthesis of Au Nanoparticles (AuNPs).

AuNPs were synthesized according to the Frens' method¹. Briefly, 15 nm Au seeds were first synthesized, 98.9 mL of water and 1 mL of trisodium citrate (30 mg/mL) were added into a conical flask on a hotplate set to 300 °C and heated to boil with gentle stirring. 0.1 ml of 98.5 mg/mL $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ was quickly added and keep boiling under vigorous stirring for seven minutes. The solution turned purple after 1 minute and turned red after 4 minutes, then cooling on ice. The AuNP sols with the size of 15 nm was prepared. The bigger diameter AuNP sols were synthesized via hydroxylamine hydrochloride reduction method². First, 1 mL of above AuNP sols and 37.4 mL of water and 0.4 mL of 100 mM $\text{NH}_2\text{OH} \cdot \text{HCl}$ and 0.4 mL of 10 mg/mL trisodium citrate were mixed in a flask under magnetic stirring (650 rpm) during 5 min, then the 0.8 ml of 1% (w/v) $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ was added and keep stirring for 1 h. AuNPs with a particle size of more than 80 nm were obtained.

Synthesis of Ag Nanowires (AgNWs).

Uniform Ag nanowires with an average diameter of 60 nm were prepared by the polyol process method³. Typically, 5.86 g polyvinyl pyrrolidone (PVP) was added to 190 mL of glycerol in a 500 mL round-bottom flask. The mixture formed a homogeneous solution under gentle stirring and then cooled down to room temperature. Afterwards, 1.58 g Ag nitrate powder was added to the solution, followed by adding a 10 mL glycerol solution containing 59 mg of NaCl and 0.5 mL of H_2O . The flask was then immersed in Oil bath with a magnetic stirrer. The solution was heated from room temperature to 210 °C under gentle stirring (50 rpm) in 20 minutes. The color of the solution turned from pale white into light brown, red, dark gray, and eventually gray-green, indicating the formation of nanowires. The heating was stopped immediately when the temperature reached 210 °C and then naturally cooled to room temperature. Finally, the excess PVP was removed by centrifuge (8000 rpm), and then the Ag nanowires were collected and dispersed into 8 times

the volume of ultra-pure water.

Self-Assembly of 3D Au-Ag plasmonic arrays

100 ml of prepared AuNP sols and AgNW sol were added with 0.2 ml of 10^{-4} M 4-NTP and incubated overnight. 1 ml of chloroform, 1 ml of AgNW sol modified with 4-NTP, 0.5 ml of AuNP sol treated in the same way and moderate amount of water was mixed in a 10 ml glass bottle. Afterwards, by shaking vigorously for ten seconds, the nanoparticles were simultaneously self-assembled into a large scale closely-packed 3D mirror film. A small amount of ethanol can be added to induce the formation of plasmonic film. Discard the supernatant, re-add the water to shake, and remove the supernatant again and repeat several times to remove the excess 4-NTP.

In Situ SERS Monitoring of the Reduction of 4-NTP on Au-Ag plasmonic arrays

For the direct observation of the reduction of 4-NTP by SERS, exploring the problem that needs to be verified by changing different conditions to the above system. Such as the sort and concentration of halogen ions, concentration of protons, etc. Afterwards, the formed three-dimensional spherical array was transferred from the glass bottle to the quartz cuvette for SERS monitoring by a portable Raman instrument. Then SERS spectra were collected directly from the surface of the 3D film-like assembly at different reaction times. Integration time in all experiments was 8 s at 90 mW incident laser power.

In Situ SERS Monitoring of the Reduction of 4-NTP in mixed AuNPs and AgNWs sol

First, The functionalization of the AuNPs and AgNWs was achieved by immersing them in an aqueous solution of the 4-NTP molecules. Typically, 0.2 ml aqueous solution (10^{-5} M) of the probe molecules was added into 10 ml of the AuNPs and three times-washed AgNWs suspension, respectively, then kept in dark for overnight to let the 4-NTP molecules chemically adsorbed on to the surface of nanoparticles. Afterwards, the nanoparticles were washed with water to remove the free 4-NTP molecules in solution. The UV absorption is the same as before centrifugation. 1 ml of functionalized AgNWs and 0.5 ml AuNPs are concentrated to 0.9 ml of mixed solution, then 0.1 ml of 1 M NaCl was added to induce the aggregation of nanoparticle. Raman

spectra were performed on B&W Tek portable Raman spectrometer at 785 nm laser excitation. And experiment and spectral acquisition conditions are the same as the SERS monitoring of the Reduction of 4-NTP on Au-Ag plasmonic arrays.

The etching of single AgNW

Freshly synthesized silver nanowires modified with 4-NTP molecules were drop-cast on clean glass slides until dry, then was performed on a Lab-RAM HR800 spectrometer (with 100x objective) with a 633 nm laser excitation source. In some cases, Milli-Q water was dropped on top under 50x objective. The laser beam (continuous wave 633 nm laser) was focused at specific positions on AgNW (usually at the middle part of one AgNW) for 20 min. Then the morphology of AgNW was observed in situ under 100 x objective after evaporation of water. The laser focal spot on the metal surface was about 1 μm in diameter with a measured power of 2-3 mW.

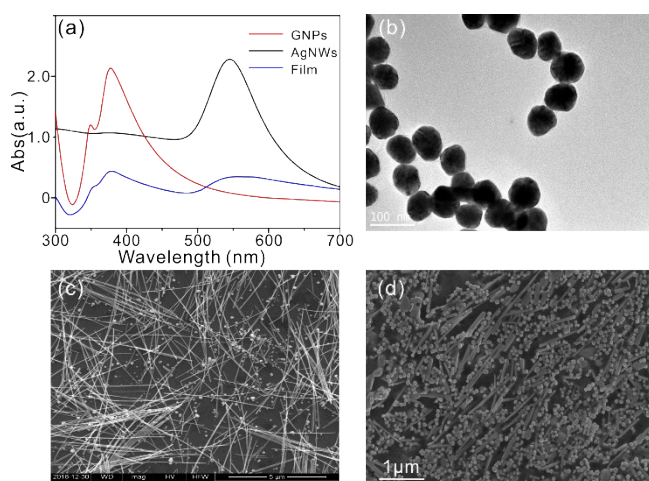


Figure S1. (a) UV-vis absorption spectra of 84 nm AuNPs (red line), AgNWs (black line) and co-assembled AgNW/AuNP films (blue line) formed by shaking. (b) TEM image of 84 nm AuNPs. (c) (d) SEM images of AgNWs and co-assembled thin films formed by shaking the mixture of 0.2 ml of AuNP sol, 0.2 ml of AgNW sol and 1 ml of chloroform.

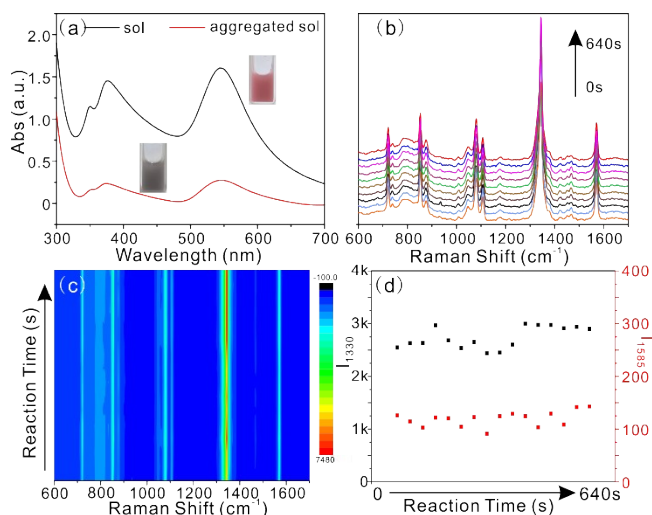


Figure S2. UV-vis absorption spectra of AuNP and AgNW sol (black line) and corresponding salt-induced aggregated sol (red line). (b) Time-course SERS monitoring on direct photoreduction of 4-NTP in aggregated AuNP and AgNW sol. (c) 2D SERS mapping for spectral calibration. (d) Time-course relative SERS intensity at 1330 cm^{-1} assigned to 4-NTP and 1585 cm^{-1} assigned to 4-ATP, respectively.

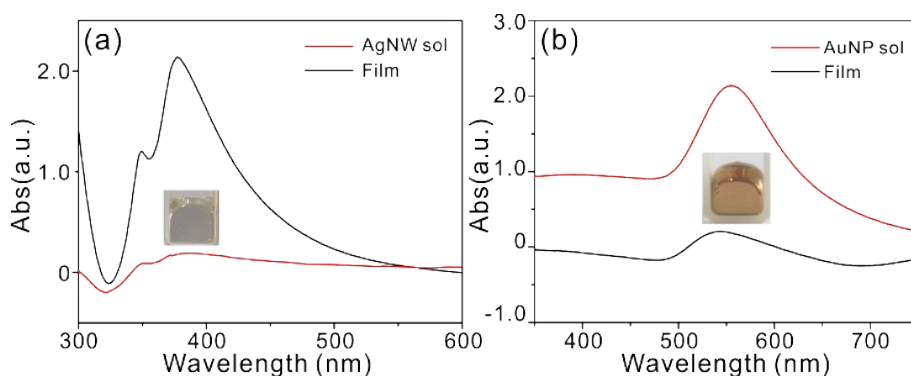


Figure S3. (a) UV-vis absorption spectra of AgNW sol (red line), co-assembled AgNW films (black line) and Corresponding optical picture. (b) UV-vis absorption spectra of AuNP sol (red line), co-assembled AuNP films (black line) and Corresponding optical picture.

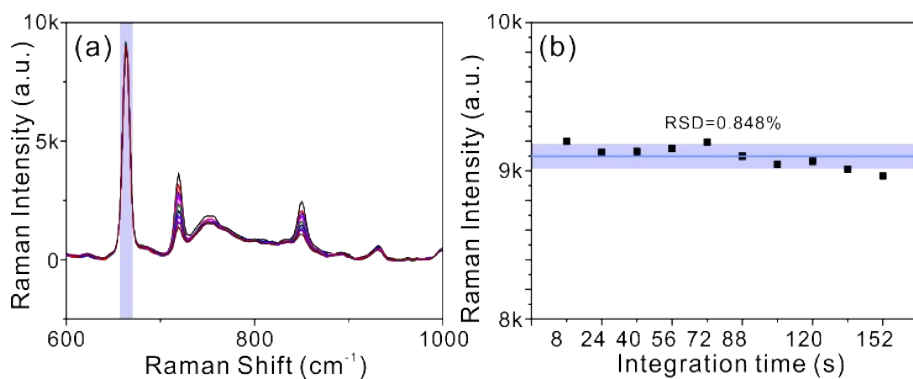


Figure S4. (a) The spectra of chloroform collected on 3D Au-Ag plasmonic arrays (The band at 662 cm^{-1}). (b) Scatter plot of the intensity of band at 662 cm^{-1} with the extension of reaction time and corresponding RSD.

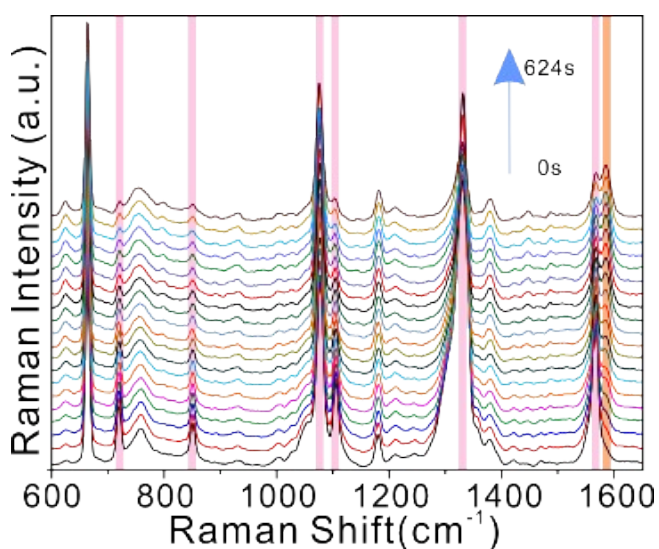


Figure S5. Time-dependent SERS spectra showing hot electron-induced reduction of 4-NTP recorded from 3D Au-Ag plasmonic arrays at liquid-liquid interface. (The peak of the pink shaded ascribe to 4-NTP, and the orange ascribe to 4-ATP). All of spectra were recorded with acquisition times of 8 s, 90 mW incident laser power, and at 785 nm excitation.

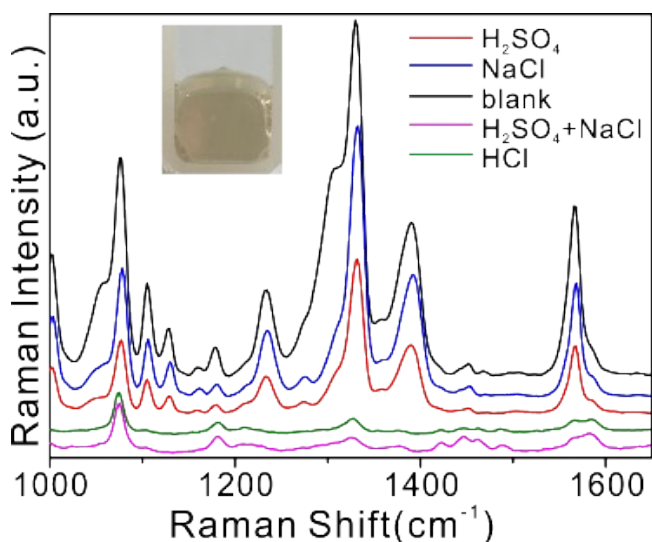


Figure S6. The SERS spectra of 4-NTP on the surface of 3D Ag plasmonic arrays in different environments. The reaction time is 400 s. Spectral acquisition conditions are the same as before.

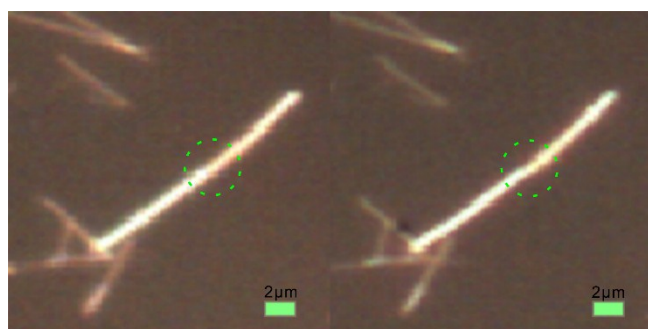


Figure S7 Optical images of a single AgNW after 10 min (left) and 25 min (right) laser illumination at aqueous solution and glass interface, respectively. (Excitation optical density was $2\text{-}3\text{ mW}\mu\text{m}^{-2}$).

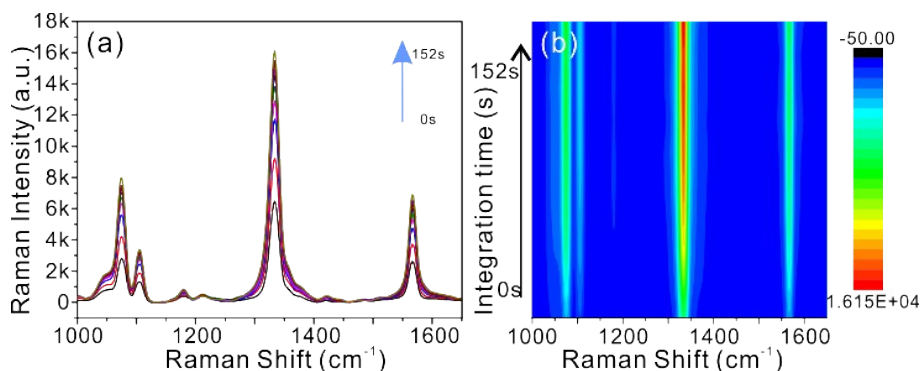


Figure S8. The SERS spectra of 4-NTP on the surface of 3D Au-Ag plasmonic arrays without the condition of halogen ion with the extension of reaction time and (b) corresponding 2D spectral mapping. Spectral acquisition conditions are the same as before.

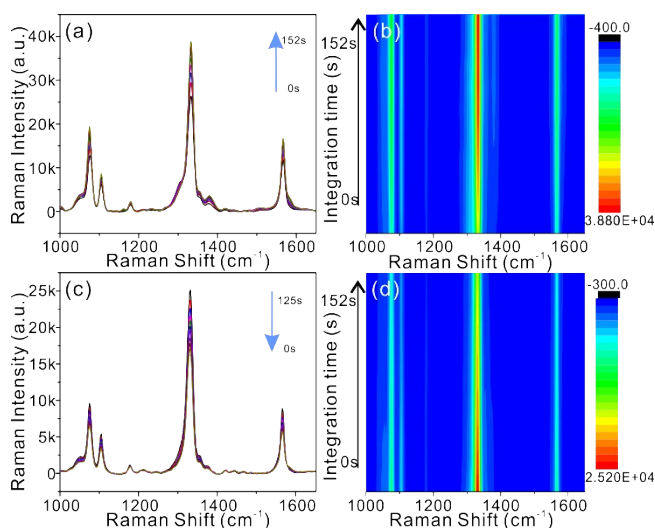


Figure S9. The SERS spectra of 4-NTP on the surface of 3D Au-Ag plasmonic arrays with the concentrations in Br are (a) 10^{-6} M, (c) 10^{-4} M and (b) (d) corresponding 2D spectral mapping, respectively. Spectral acquisition conditions are the same as before.

Reference

1. G. Frens, *Controlled Nucleation for the Regulation of the Particle Size in Monodisperse Gold Suspensions*, Macmillan company, 1973.
2. W. Haiss, N. T. Thanh, J. Aveyard and D. G. Fernig, *Analytical Chemistry*, 2007, **79**, 4215-4221.
3. C. Yang, H. Gu, W. Lin, M. M. Yuen, C. P. Wong, M. Xiong and B. Gao, *Advanced Materials*, 2011, **23**, 3052.