# Hybrid single visible nanoreactor for in situ SERS monitoring of plasmon-

## driven and small Au nanoparticles catalyzed reactions

#### Experiments

#### Materials

Toluene, NaBH<sub>4</sub>, AgNO<sub>3</sub> (99+ %) and poly(vinyl pyrrolidone)(K-30) were purchased from Sinopharm Chemical Reagent Co. Ltd. China. Ethylene glycol (anhydrous, 99.8%), 4aminothiophenol (4-ATP) and crystal violet (CV) were purchased from Sigma-Aldrich. All chemicals used in this study were of analytical grade. HAuCl<sub>4</sub>•3H<sub>2</sub>O was obtained from Shanghai Chemical Co. Ltd. China. Tetraoctylammonium bromide (TOAB) was purchased from Adamas Reagent Co. Ltd. Dimethylaminopyridine (DMAP) was purchased from K Chemical Ltd. All the solutions were prepared in double distilled water.

#### Synthesis of positive charged Au NPs

The synthesis was carried out according to the literature<sup>1</sup> with a small modification. A typical experiment to synthesize positive charged Au NPs was as follows: 7.4 mL HAuCl<sub>4</sub> (1%) solution was added to a solution of tetraoctylammonium bromide (25 mM) in toluene (16 mL). The transfer of the metal salt to the toluene phase can be clearly seen visually within a few seconds. Following, the freshly prepared 5 mL NaBH<sub>4</sub> (0.4 M) was added to the stirred mixture, which caused an immediate reduction to occur. After 30 min the two phases were separated and the toluene phase was subsequently washed with H<sub>2</sub>SO<sub>4</sub> (0.1M), NaOH (0.1 M) and H<sub>2</sub>O (three times). An aqueous 0.01M 4-dimethylaminopyridine (DMAP) solution (1 mL) was added to aliquots (5 mL) of the asprepared nanoparticles mixtures, and set for 12 h. Then the Au NPs was transferred from organic phase to aqueous phase. Finally, after removing the organic phase, the aqueous phase was diluted to 10 mL with ultra-pure water.

#### Synthesis of negative charged Ag NWs

The synthesis was carried out according to the literature.<sup>2</sup> Briefly, EG (10 mL) was firstly refluxed in a three-necked round-bottom flask at 160°C for 2 h, and then 5 mL EG solution of 0.1M AgNO<sub>3</sub> and 5 mL EG solution of 0.2M poly(vinyl pyrrolidone) (PVP, K-30) were simultaneously injected into the refluxing solvent, at a rate of 0.2 mL/min. The reaction continued at 160°C for 60 min. Finally, the 1mL as prepared Ag NWs was washed with acetone (9 mL) for 2 times, and water (10 mL) for 3 times.

#### Preparation of Ag NW-Au NPs hybrid nanostructure

1 mL as-prepared positive charged Au NPs was mixed with 10 mL as-prepared negative charged Ag NWs. After standing for about 30 min, the hybrid Ag NW- Au NPs was obtained and can be directly used as both SERS substrate and catalyst after removing the redundant Au NPs though centrifuge.



**Fig.S1** The self-assembled of single nanoreactor Ag NW-Au NPs using the electrostatic adsorption. **Characterization and instruments** 

UV-vis absorption spectra were recorded using a Shimadzu UV-2550 spectrophotometer (Japan). Scanning electron microscope (SEM) images were acquired with field-emission scanning microscopy (FE-SEM, Siron 200) at an accelerating voltage of 10 kV. Transmission electron microscopy (TEM) images were recorded by a JEOL 2010 high resolution transmission electron microscope equipped with an Oxford INCA energy dispersive spectroscopy (EDS) system at an accelerating voltage of 200 kV. SERS measurements were performed with a Lab RAM HR800 confocal microscope Raman system (Horiba Jobin Yvon) using a He-Ne laser operating at 632.8 nm. The laser beam was focused on the sample of a size of about 1 mm using a 50 × microscope objective.



**Fig.S2** (A) UV-vis spectra of Au NPs, Ag NWs and the hybrid superstructures Ag NW-Au NPs, respectively; (B) SEM image of ensemble Ag NW-Au NPs.

UV-vis extinction spectra also showed various plasmon resonances and the corresponding

couplings in Fig.S1A. As-synthesized Ag NWs presents two peaks at 350 nm and 380 nm. A maximum at 520 nm can be attributed to Au NPs. Because of Au NPs coating on Ag NWs, the peak at 550 nm which was attributed to tethered Ag NPs red-shifted from the relative to the 520 nm SPR peak of Au NPs suspension. Obviously, the absorption spectrum of Ag NW-Au NPs composite is different from the direct sum of the absorption spectra of Au NPs and Ag NWs. That is, the very broad maximum covering the 500-700 nm ranges was strongly dependent upon coupling of Au NPs and Ag NWs interactions, which is consistent with the results of DFM. Fig.S1B exhibits the hybridized structures in large yield after washing several times with water.



**Fig.S3** The element mapping (A) Ag, (B) Au and (C) the corresponding energy dispersive spectroscopy (EDS) spectrum of hybrid structures Ag NW-Au NPs, respectively.



Fig.S4 The SERS spectra of CV (10<sup>-7</sup>M) using different structure as SERS substrate.



**Fig.S5** (A) Optical photograph of Ag NW-Au NPs under the microscopy coupled to Raman instrument with a 50×objective; (B) SERS mapping of Ag NW-Au NPs at peak 1172 cm<sup>-1</sup> with 0.5 $\mu$ m/point scan step and an area of 6×12  $\mu$ m<sup>2</sup>.



**Fig.S6** (A) The time-dependent SERS spectra and (B) the rate constant of different band for the plasmon-driven reaction of 4-NTP dimerizing into DMAB during 300 s using the single Ag NW substrate as well as surface plasmon. The spectra were collected with an integrate time of 1 s under continuous 632.8 nm laser exposure, and the laser power of 1 mW.



**Fig.S7** (A) The time-dependent SERS spectra and (B) the rate constant of different band for the plasmon-driven reaction of 4-NTP dimerizing into DMAB during 300 s using the single Ag NW-Au NPs SERS substrate. The spectra were collected with an integrate time of 1 s under continuous 632.8 nm laser exposure, and the laser power of 2.5 mW.



**Fig.S8** (A) The time-dependent SERS spectra and (B) the rate constant of different band for the plasmon-driven the reaction of 4-NTP dimerizing into DMAB during 300 s using the single Ag

NW-Au NPs substrate. The spectra were collected with an integrate time of 1 s under continuous 632.8 nm laser exposure, and the laser power of 0.1 mW.

### References

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