Electronic Supplementary Material (ESI) for Chemical Communications


## Electronic Supplementary Information (ESI) for

# On-chip fabrication of silver microflower arrays as a catalytic microreactor for allowing in-situ SERS monitoring†

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## Experimental

### Preparation of silver precursor

In a typical synthesis of the transparent silver-precursor solution, 0.08M silver nitrate ($AgNO_3$) aqueous solution and 0.06 M trisodium citrate ($C_6H_5O_6Na_3$) were mixed under stirring at room temperature. Then proper amount of aqueous ammonia was dripped into the mixture until a clear solution was obtained.

### Preparation of microfluidic chip

The microchannel was fabricated on a normal glass substrate using the combination of photolithography and wet-etching techniques. Briefly, a glass slide was washed by acetone, alcohol and deionized water, and then dried by nitrogen. After deposition of Chrome (30 nm, adhesive layer) and gold (100 nm, sacrificial layer) on the glass slide, a layer of photoresist was spin coated on the sacrificial layer (SL). Required channel patterns could be obtained by ultraviolet exposure under a mask and subsequent development. After orderly removal of exposed SL and then photoresist film, the glass slide was etched by hydrofluoric acid. Finally, a glass chip with channels imbedded was finally obtained. Before usage, the chip was cleaned ultrasonically by acetone and alcohol for ten minutes, respectively. Then it was further rinsed by distilled water and dried with nitrogen gas.
PDMS microchannel was prepared by soft lithography from the glass microchannel.

### Fetmosecond laser fabrication of SERS substrates in microchannel

For fabrication of silver microflower arrays in the microchannel, a femtosecond laser pulses with central wavelength of 800 nm; pulse width of 120 fs; and repetition rate of 80 MHz was tightly focused into the silver precursor by a 100×oil immersion objective lens with a high numerical aperture (NA=1.40). The focal spot was scanned laterally by steering a two-galvano-mirror set and keeping along the optical axis by a piezo stage, both with high motion accuracy. The silver microflower arrays were fabricated under the condition of 10-20 mW laser power before the objective lens and of from 1000 μs to 2000μs exposure duration at each dot. The equal-arc combining equal-height in numerical simulations and data processing were used to fabricate microflower. In general, the scanning route was a spiral mode in each equal-height face. All the process of fabrication was controlled by computer exactly. The patterned silver microflower arrays were rinsed in distilled water for 10 min to remove the residual silver-ion solution. For the typical fabrication of 4*50 silver microflower arrays, it will cost ~6 hour. The processing time further depends on the step length and exposure duration.

### Preparation of the catalytic micro-reactor

For the preparation of catalytic micro-reactor, the silver microflower arrays functionalized “Y” channel was sealed with a PDMS slice. Then three pools including two inlet and one outlet pores were made on the PDMS slice. Two injection pools was controlled by micro-pump, the outlet of the channel was connected to a container to collect the products.

### Characterization

The absorption spectra were measured on a Shimadzu UV-3600 spectrometer. The surface morphologies of the samples were measured on a JEOL JSM-6700F field emission scanning electron microscope (FE-SEM) operating at 3.0 keV. The the crystalline stucture of the samples were characterized through JEOL-2100F high-resolution transmission electron microscope (HRTEM) at 200 kv. XRD pattern was collected on a Rigaku D/MAX 2550 diffractometer with CuKα radiation (λ=1.5418). X-ray photoelectron spectroscopy (XPS) was performed using an ESCALAB 250 spectrometer. Surface-enhanced Raman spectra were measured on JOBIN YVON T64000 equipped with a liquid-nitrogen-cooled argon ion laser at 524.5 nm (Spectra-Physics Stabilite 2017) as excitation source (the laser power used was about 40 μW at the samples with an average spot size of 1 μm in diameter). The spectral resolution was 4 $cm^{-1}$ at the excitation wavelength.

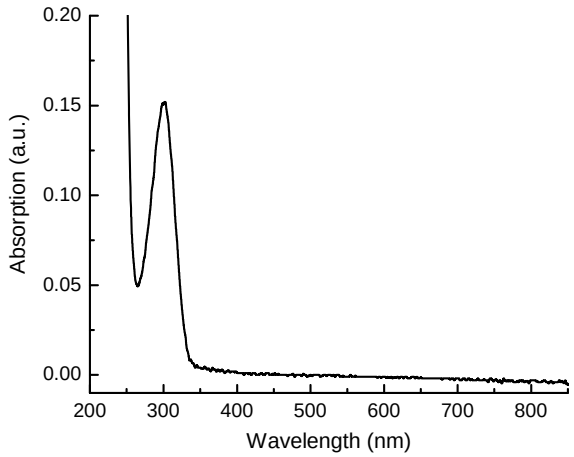


**Fig. S1** Absorption spectrum of silver precursor used for laser processing.

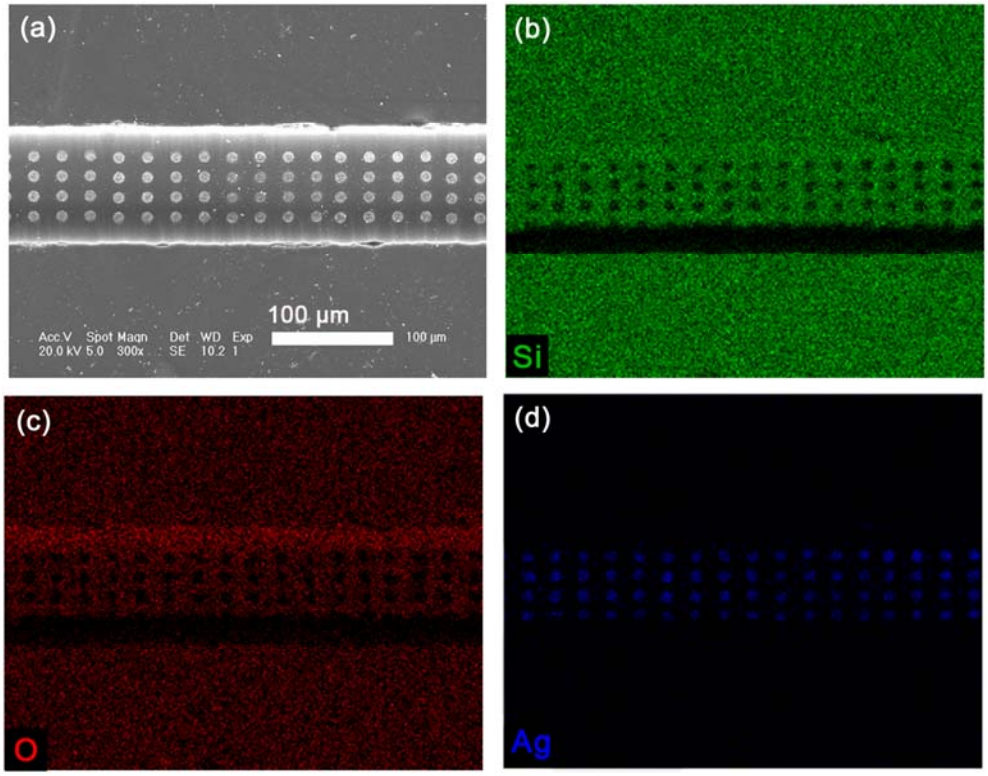


**Fig. S2** SEM image and elemental maps of the microchannel with silver microflower arrays. (a) SEM image, (b) Si map, (c) O map. (d) Ag map.

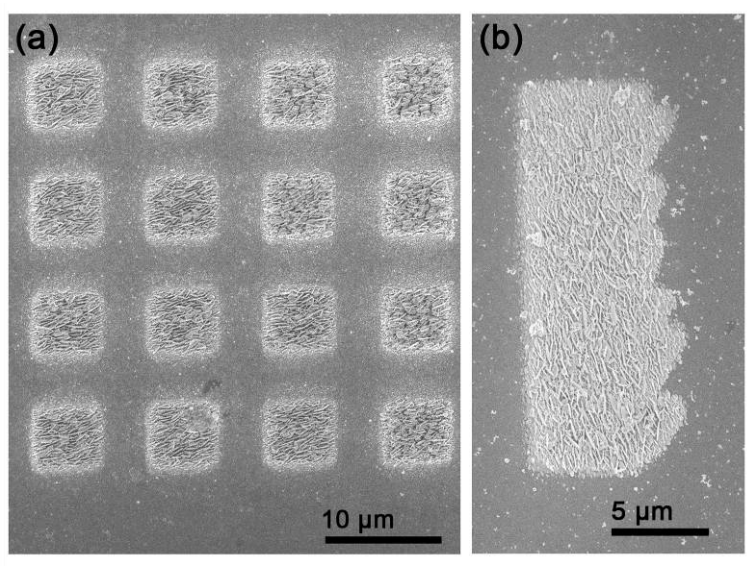


**Fig. S3** (a) SEM image of silver square microarrays. (b) SEM image of silver patterns with irregular edges.

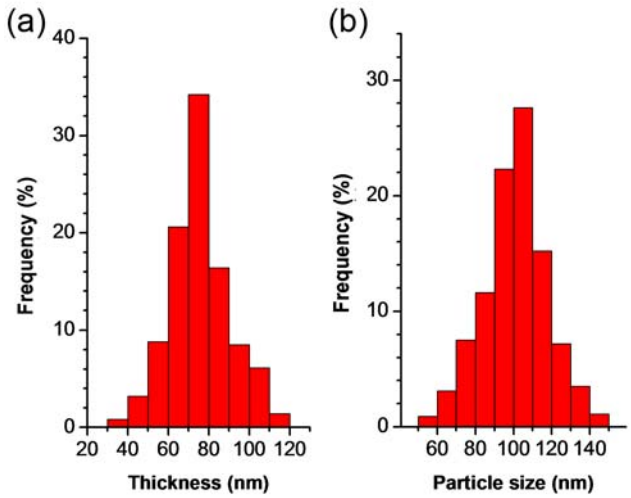


**Fig. S4** Statistic results of the average thickness of the nanoplates and the size distribution of the attached nanoparticles

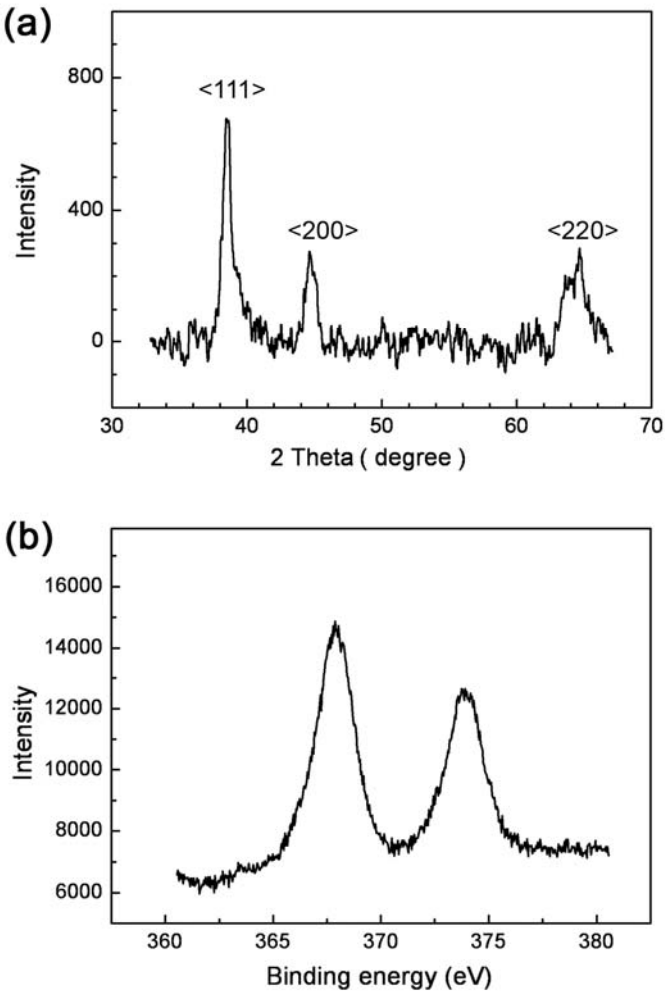


**Figure S5.** (a) XRD pattern of the silver substrate. (b) XPS spectrum of the silver substrate.

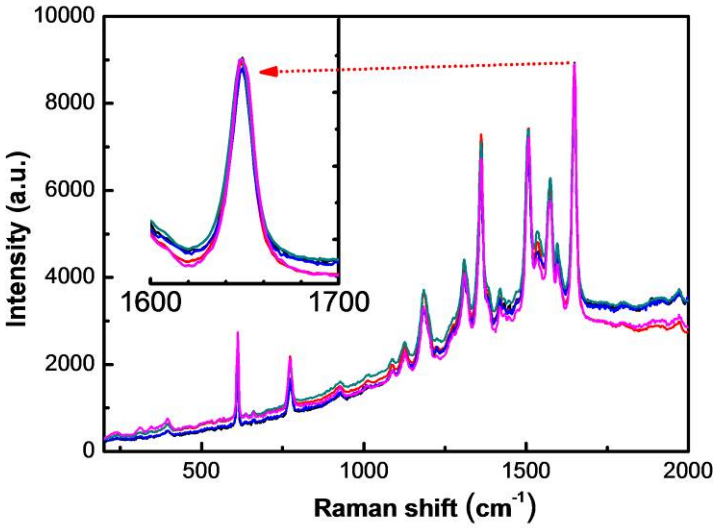


**Fig. S6** Raman spectra of R6G detected at five different silver microflowers. The inset is the magnified spectra of the peak at ~1650 $cm^{-1}$.

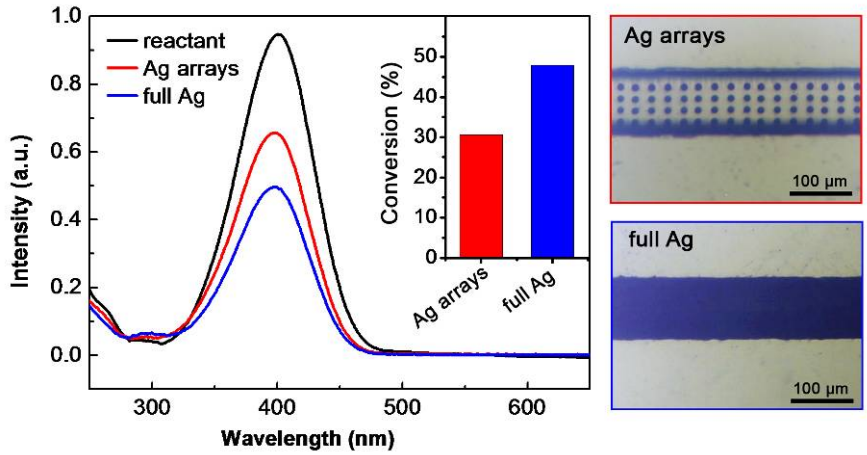


**Fig. S7** Absorption spectra of the collected products from the catalytic microreactors of Ag arrays and full Ag, the flow rate is 8 mL/h. Inset is the conversion of 4-nitrophenol over the two microchannels. The right images are optical microscopic images of the two microchannels.

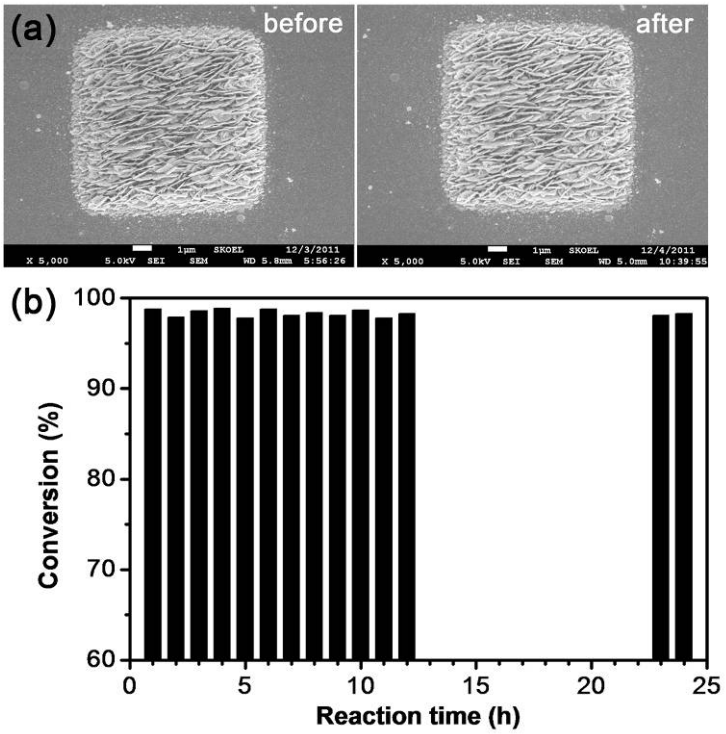


**Fig. S8** (a) SEM images of a silver square before and after microfluids impingements for 24h (flow rate: 10mL/h). (b) Catalytic activities of the silver microflower arrays during continuous reaction for 24h.

## Estimation of enhancement factor

Taking P-aminothiophenol (p-ATP) as test molecules, the enhancement factor (EF) of the samples was estimated, in order of magnitude, by the equation:

$$\mathbf{EF = (I_{SERS}/N_{ads})/(I_{bulk}/N_{bulk})} \quad [s1]$$

Where $I_{SERS}$ and $I_{bulk}$ are the Raman signals at a certain vibration for the p-ATP molecules adsorbed on a substrate with SERS effect and solid p-ATP molecules, respectively. $N_{ads}$ and $N_{bulk}$ are the numbers of the adsorbed and the solid p-ATP molecules within the laser spot, respectively. In our experimental condition for solid p-ATP, the probe volume could be considered to be a tube with a waist diameter of ~ 1.0μm and a depth of ~ 20μm. So we can calculate the $N_{bulk}$ value, about $9.4\times10^{10}$. The $N_{ads}$ can be calculated by dipping definite volume p-ATP/ ethanol solution (0.1 nM) on the substrate, estimating the existing area and the amount of molecule in the laser dot can be attained. We estimate the EF value, for the vibration at 1075 cm-1.

$$\mathbf{EF=4\times10^{8}}$$

[s1]Orendorff C J, Gole A, Say T K and Murphy C J, Anal. Chem 2005, 77, 3261-3266.