

*Electronic Supplementary Information*

**Automatic molecular collection and detection by using  
fuel-powered microengines**

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## 1. Experimental procedures

Au/SiO/Ti/Ag microengines were fabricated by roll-up nanotechnology. The procedure was initiated by spin-coating a photoresist layer (ARP-3510T positive resist) with a thickness of  $\sim 2.5\mu\text{m}$  onto a silicon substrate. Standard photolithography was employed to pattern the photoresist layers into well-defined squares. Subsequently, different materials were deposited on the photoresist layer by electron beam evaporation with a tilt angle of  $30^\circ$ , where their thicknesses nominally are 5/10/10/7 nm for Au/SiO/Ti/Ag and the Au layer thickness was varied for optimized detection performance. By employing such a glancing angle deposition technique, a predefined rolling direction of the nanomembrane was introduced. Ultimately, the photoresist layer was selectively removed by acetone. Simultaneously, intrinsic stress gradients across the deposited layers acted as a driving force to precisely release nanomembranes into rolled-up microengines. The microengines were dried in the critical point dryer (Leica, CPD030) by using liquid  $\text{CO}_2$  as intermedia to avoid collapse.

The microengines were placed on several clean silicon wafers. Freshly prepared different concentrations of  $\text{H}_2\text{O}_2$  solutions (0%, 0.73%, 3.64%, 7.28%) containing  $10^{-6}$  M Rhodamine 6G were slowly dispensed on the wafers. A trace amount of surfactant (0.01 wt% sodium dodecyl benzene sulfonate) is also necessary to avoid huge bubbles. Concentration of microengines in the fluids was approximately  $490\text{ ml}^{-1}$ . In order to allow molecule adsorption, all the samples were maintained for 30 min without agitation in room temperature and then transferred to the drying oven ( $40^\circ\text{C}$ ) for drying process.

## 2. Characterizations

Scanning electron microscopy (SEM, FEI Inspect F50) was used to investigate the microengines. Atomic force microscopy (AFM, MultiMode) was employed to illustrate the surface. Raman measurements were performed with a Renishaw (inVia) Raman spectrometer using a 514-nm laser line at room temperature. An area  $\sim 1\mu\text{m}$  in diameter was probed with a  $50\times$  objective lens, and the incident power at the sample

was 0.05 mW. The signal collection time was 20 s. The Raman data were processed by a commercial software named NGSLabSpec. The function of “baseline correction” was applied to remove the fluorescence signals of R6G. The SERS map with an area of  $81.0 \times 57.0 \mu\text{m}^2$  (Fig. 2d) was achieved by measuring 560 points at a regular scanning step of  $3.0 \mu\text{m}$ . The intensity of 3000 (a.u.) was set as maximum of the scale bar and the intensity of 400 (a.u.) was set as minimum of the scale bar. An optical microscope (Olympus BX51) with an integrated high-speed camera was adopted to capture the locomotion of the microengines.

FDTD simulation was applied to calculate the electromagnetic (EM) field properties. The Drude model was employed to describe the properties of metal (Au). The parameters of the nanostructure in the simulation were set to the parameters in our experiments, and the structure is illuminated by an incident plane wave at the wavelength of 514 nm in the simulation. Because of light absorption of metal layers (e.g. Au and Ag), detecting depth of the laser is limited. Thus the influence from the silver layer was not counted in the simulation. Furthermore, the structure is illuminated by an incident plane wave at the wavelength between 400 to 700 nm in the simulation to verify the relationship between the enhancement and wavelength (Figure S1), which indicates that the wavelength of 514 nm is suitable for the LSPR of the structure.

### 3. SERS Enhancement Factor (EF) Calculation

#### 3.1 Theoretical EF (TEF) Calculation

The SERS TEF is estimated by a simplified approximation according to the following equation:

$$\text{TEF} = \frac{E_{\text{loc}}^4}{E_0^4}$$

where  $E_{\text{loc}}$  is the location electric-field intensity, and  $E_0$  is the electric-field intensity associated with the incident plane wave. For largest enhancement in the simulation,  $E_{\text{loc}} = 18 \text{ v/m}$ ,  $E_0 = 1.0 \text{ v/m}$ .

### 3.2 Empirical EF (EEF) Calculation

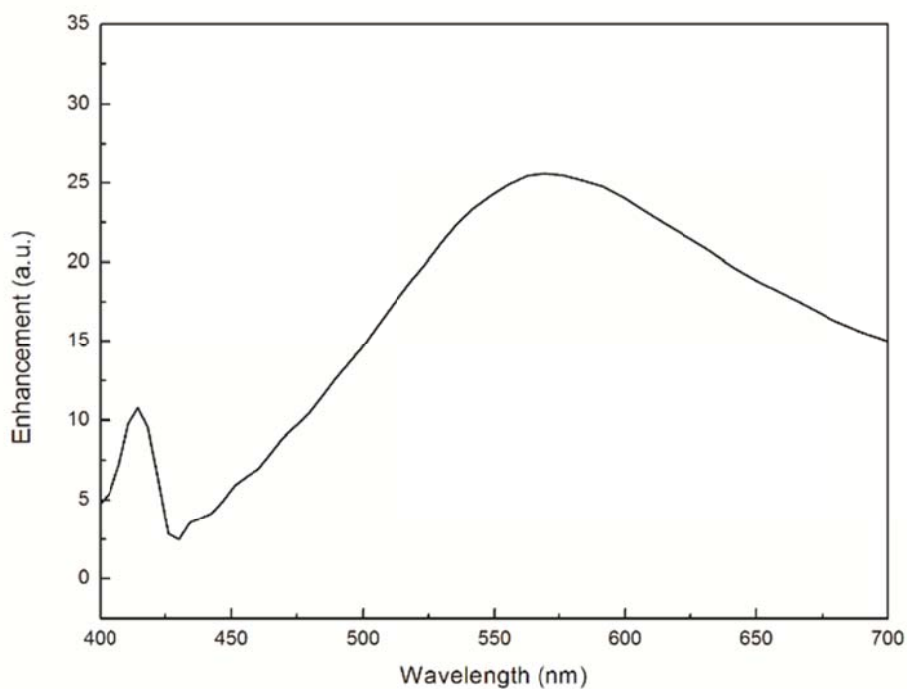
The SERS EEF is estimated by comparing the ratios of the average SERS peak intensity at  $1650\text{ cm}^{-1}$  of the probe molecules to the corresponding average unenhanced signals contributed by a surface-adsorbed molecule according to the following equation:

$$EEF = \frac{I_{SERS}/N_{SERS}}{I_{Raman}/N_{Raman}}$$

where  $I_{SERS}$  and  $I_{Raman}$  represent the Raman intensities for the probe molecules on substrates surface, respectively and  $N_{SERS}$  and  $N_{Raman}$  represent the numbers of the corresponding molecules that effectively excited by the laser. The experimental conditions such as the laser wavelength, laser power, microscope objective, spot size, spectrometer, and measurement conditions on the substrate are identical in all cases.

It should be noted that the number of molecules attached to the microengines is larger than the analyte concentration in the fluid. However, in order to comprehensively test the molecules collecting system, the concentration of analyte in the fluid ( $10^{-6}\text{ M}$ ) is used to calculate EEF.

For largest enhancement, Au/SiO/Ti/Ag microengines collected in the fluid (3.64%  $\text{H}_2\text{O}_2$ ) has the parameters:  $I_{SERS} = 3269.3$ ,  $N_{SERS} = 10^{-6}\text{ M}$ . While a gold sheet reference has the following parameters:  $I_{Raman} = 625.5$ ,  $N_{Raman} = 10^{-1}\text{ M}$ . Thus the SERS EEF is estimated to be larger than  $5 \times 10^5$ .



**Figure S1.** The relationship between the enhancement and wavelength in FDTD simulation.

Point	1	2	3	4	5	6	7	8	9	10	Mean	Std dev
Case i	2081	2723	5692	5633	2610	4205	2340	2516	2635	2259	3269	1388
Case ii	426	588	1091	933	565	836	1083	660	606	661	745	229
Case iii	734	541	907	967	614	555	497	816	487	750	687	173

**Table S1.** Statistical data of R6G Raman signal intensity (a.u.) at  $1650\text{ cm}^{-1}$  in different cases.

Point	1	2	3	4	5	6	7	8	9	10	Mean	Std dev
0.73%	1310	2018	1435	1545	1121	1172	979	1017	1038	1444	1308	318
3.64%	2081	2723	5692	5633	2610	4205	2340	2516	2635	2259	3269	1388
7.28%	743	806	484	503	1127	1663	859	498	587	674	794	365

**Table S2.** Statistical data of R6G Raman signal intensity (a.u.) at  $1650\text{ cm}^{-1}$  in different fuel concentrations.

#### 4. Videos

**Video S1:** The trajectory of a microengine in a concentration of 3.64% H<sub>2</sub>O<sub>2</sub> fuel containing 10<sup>-6</sup> M R6G.

**Video S2:** The trajectory of a microengine in a concentration of 0.73% H<sub>2</sub>O<sub>2</sub> fuel containing 10<sup>-6</sup> M R6G in 7.5s.

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