

1 **Electronic supplementary information:**

2 **Fabrication of plasmonic opposite metal spindles in**  
3 **nanowells by shadow deposition for sensing**

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10 **Contents**

11 Detailed experimental section;

12 Scheme of the fabrication of the mold for NIL;

13 SEM images of the mold and PMMA nanowells;

14 The detailed parameter of samples;

15 Distribution of EF of sample A.

## 1 **Experimental section**

### 2 **Chemicals and materials**

3       Chemicals and solvents of reagent quality were used without further  
4 purification. Analytical reagent-grade ethanol, acetone, chloroform, sucrose  
5 were purchased from commercial sources. The PMMA powder (molecular  
6 weight  $M_w=96700$ ), tridecafluoro-1, 1, 2, 2,-tetrahydrooctyl-trichlorosilane,  
7 rhodamine 6G and the Au wire (99.999%) were purchased from Sigma-Aldrich.  
8 The monodispersed PS spheres of 538 nm in diameter with less than 5%  
9 diameter variation were obtained from Wuhan Tech. Co.. The quartz slices and  
10 one side polished n-type (100) oriented Si wafers were obtained from Beijing  
11 Zhongjingkeyi Tech. Co., China.

### 12 **Preparation of nanopillar mold**

13       The Si wafer was cut into  $1 \times 1$  cm<sup>2</sup> slices and subsequently cleaned by sonicating  
14 in acetone, chloroform, ethanol and deionized water for 3 min respectively to remove  
15 organic contaminants. Then the Si slides were dried under nitrogen gas flow before  
16 use. A monolayer of PS spheres was prepared onto the Si slices. An reactive ion  
17 etching (RIE) process was conducted to reduce the diameter of PS nanospheres on a  
18 Plasmalab 80 Plus (ICP65) system (Oxford Instruments Co., UK). The etching time  
19 was 8 min under a RF power of 30 W, an ICP power of 30 W, a pressure of 40 mTorr  
20 and O<sub>2</sub> flow rate of 20 sccm. Then the residual PS nanospheres were used as masks  
21 for creating Si nanopillars with RIE. The etching process was performed using a 2:15  
22 mixture gas of SF<sub>6</sub> and CHF<sub>3</sub> at total flow rate of 51 sccm, pressure of 10 mTorr, RF

1 power of 25 W and ICP RF power of 100 W. The etching time was set at 3 min. Then  
2 the residual PS nanospheres were removed by sonicating in acetone and ethanol for 3  
3 min, respectively. Then a monolayer of tridecafluoro-1, 1, 2, 2-tetrahydrooctyl-  
4 trichlorosilane was assembled on the samples by vapor phase deposition to lower the  
5 surface energy.

#### 6 **Preparation of PMMA nanowell arrays**

7 The quartz slices ( $1.5 \times 1.5 \text{ cm}^2$ ) were cleaned with acetone, chloroform and  
8 ethanol in an ultrasonic bath for 5 min respectively. A 200 nm PMMA layer  
9 was spin-coated onto the substrate. The NIL process was carried out on a 2.5-in.  
10 Nanoimprinter (Obducat AB, Malmö, Sweden). NIL process was performed at  
11 175 °C, under 30 bar for 600 s. Following the embossing time, the substrate was  
12 cooled down to 80 °C and the mold was peeled off from the PMMA layer. The  
13 residual PMMA was removed with RIE process with a gaseous of oxygen for 1  
14 min.

#### 15 **Preparation of arrays of opposite metal spindles in nanowells**

16 The arrays of opposite metal spindles were fabricated by conducting two  
17 shadow deposition processes at opposite directions on a commercial vacuum  
18 thermal evaporation system (Shenyang Keyou Institute of Vacuum Technology,  
19 China).

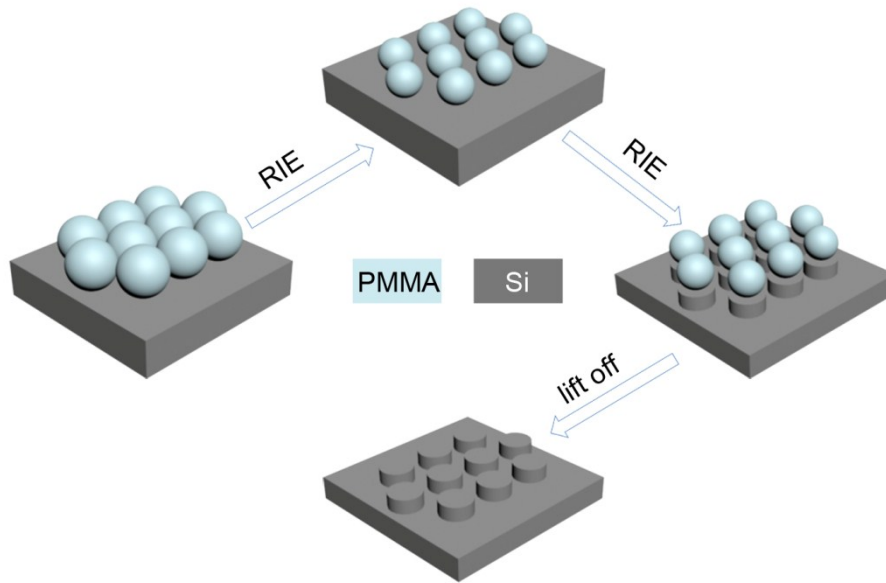
#### 20 **Characterization**

21 AFM measurements were taken on a Multimode Nanoscope instrument  
22 (Digital Instrument, USA). SEM images were taken using a Hitachi SU8020

1 field emission scanning electron microscope (Hitachi, Ltd., Japan) operated at  
2 3.0 kV. Reflection spectra were recorded on an R1-A-UV series spectroscopy  
3 meter (Shanghai Ideaoptics Instrument Co, Ltd, China). Raman spectra were  
4 measured on a system under excitation wavelength of 633 nm. The data  
5 acquisition time was set to 20 s for each measurement. A silicon wafer was  
6 used to calibrate the spectrometer.

### 7 **Finite-difference time-domain (FDTD) simulation**

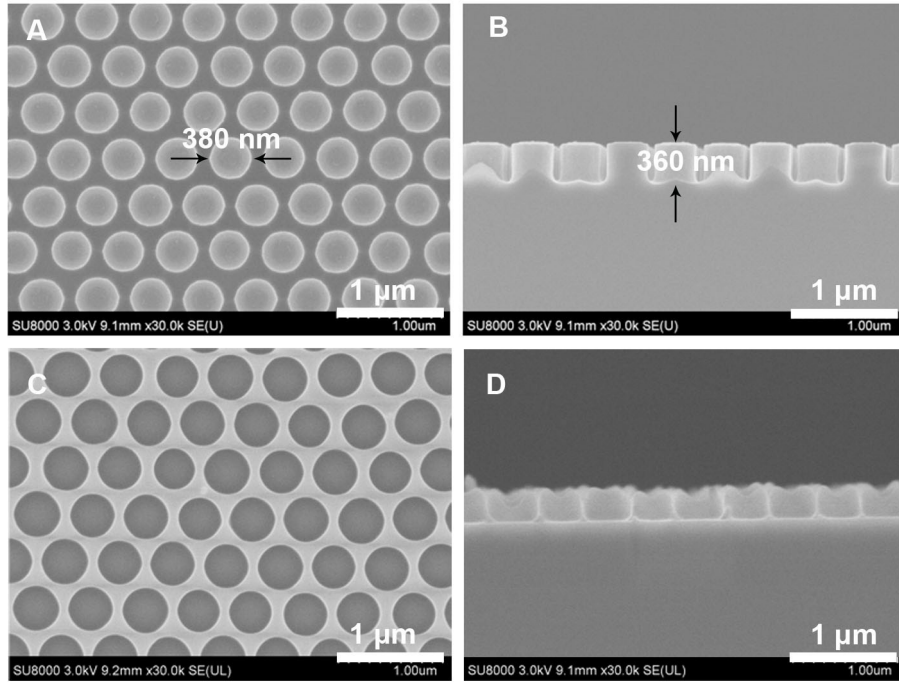
8 Lumerical FDTD Solution software was used to simulate the  
9 electromagnetic field intensity and the spectrum of the structures. The dielectric  
10 coefficients of all materials used were obtained from Palik's handbook.  
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2 **Fig. S1.** Schematic illustration of the process for fabricating Si mold.

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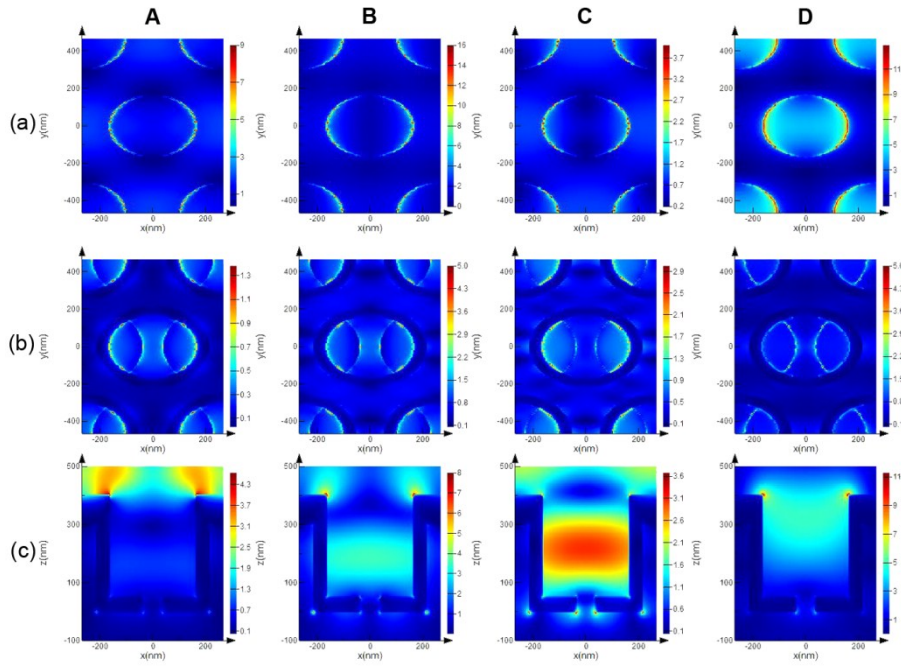
2 **Fig. S2.** (A) Top view and (B) cross-sectional SEM images of the Si mold. (C) Top  
 3 view and (D) cross-sectional SEM images of the PMMA nanowells after removing  
 4 the residual layer.

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6 Table S1. Parameters of the spindles created with different deposition angles.

	A	B	C
Deposition angle (°)	30	45	60
Long axis (nm)	330	280	250
Short axis (nm)	135	120	80
“gap” (nm)	75	100	150

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2 **Fig. S3.** The distribution of electromagnetic field of sample A at the wavelength of P1  
 3 (line A), D1 (line B), P2 (line C) and D2 (line D). Row (a) and (b) represent the  
 4 distribution of electromagnetic field of XY plane on the top and bottom of the  
 5 nanowell. Row (c) represents the distribution of electromagnetic field of XZ plane.