Electronic Supplementary Material (ESI) for ChemComm.

Ultrathin ZIF-8 Wrapping on Au-dotted Ag-Nanowire for SERS-Based CO_2 Detection: Portability, Rapidity and High Selectivity

Experimental section：

Materials and reagents

Silver nitrate ($AgNO_3$, 99.8%), methanol, ethylene glycol (EG, 99.0%), sodium chloride (NaCl), polyvinyl pyrrolidone (K-30), and $HAuCl_4$•$4H_2O$ were purchased from Shanghai Chemical Co. Ltd. China. Zn $(NO_3)_2$•$6H_2O$ and 2-methylimidazole were obtained from Shanghai Aladdin Biochemical Technology Co. Ltd. All reagents were analytical grade without further purification. Ultrapure water was used throughout the experiments.

Synthesis of Au NPs

Gold nanoparticles (Au NPs) were synthesized by a previous reported method[1]. 1mL $HAuCl_4$ aqueous solution was added to 99 mL ultrapure water. Then, 3 mL sodium citrate solution was quickly injected into the boiling $HAuCl_4$ solution and further stirring for 30 min. After cooling down, the color of the Au NPs colloid was wine red.

Preparation of Ag NWs

Silver nanowires (Ag NWs) were synthesized by a modified solvothermal polyol process[2]. Polyvinyl pyrrolidone (0.8 g) was dissolved in 20 mL ethylene glycol solution, and then $AgNO_3$ (0.6794 g) and NaCl (0.7 mg) were also added to another 20 mL ethylene glycol solution. The two solutions were mixed and stirred for 30 min. Finally, the mixture was heated to 160℃ and maintained for 2.5 h. The obtained Ag NWs were collected by centrifugation, repeatedly washed and then dispersed in methanol for further usage.

Synthesis of Ag@Au NWs

10 mL as-synthesis Ag NWs were centrifuged and then added to 85 mL Au NPs colloid. After shaking for 3 h, the products were obtained by centrifugation. Then, the products were repeatedly washed with methanol for further usage.

Fabrication of Ag@Au@ZIF-8 NWs

$Zn(NO_3)_2 \cdot 6H_2O$ (0.1859 g) and 2-methylimidazole (0.0513 g) was dissolved separately in 25mL methanol.A certain amount of $Zn(NO_3)_2$/methanol solution was added to the as-synthesis Ag@Au NWs. Subsequently, the same amount of 2-methylimidazole/methanol solution was injected into the mixture at 10℃. After 1 minute, the obtained sample was rinsed with methanol. By adjusting the concentration of the ZIF-8 precursor solution and the reaction time during the reaction, ZIF-8 shells with different thicknesses were successfully prepared (70nm, 30nm, 15nm, 5nm and 1nm).

Preparation of disordered nanowire membrane

Ag@Au@ZIF-8 nanowire membrane was made by simple vacuum filtration. And then the obtained membrane was dried at 40℃ for further use.

SERS Measurement

First, the obtained membrane was put into a sealed space filled with the mixture gas (N_2, O_2, CO_2) for some time. Subsequently, the SERS detection of the sample was quickly carried out at room temperature.

General Characterization Methods.

Scanning electron microscopy (SEM) images were acquired on a S-4800 SEM instrument (HITACHI, Japan). UV-vis spectra were obtained by using a UV-1800 spectrophotometer (Shimadzu). HRTEM images were performed on a JEM-2100 high-resolution transmission electron microscope. X-ray photoelectron spectroscopy (XPS)(ESCA Lab MKⅡ) was used to detect the chemical composition of the sample. A powder X-ray diffraction (XRD) pattern was obtained using a Philips X’Pert PRO SUPER X-ray diffractometer equipped with graphite-monochromated Cu Kα radiation (λ = 1.54056 Å). The Raman spectra were collected using a Lab RAM HR800 confocal microscope Raman system (Horiba Jobin Yvon，632.8nm) with a 50× objective lens.

The Raman spectra were collected with an acquisition time of 5 s. The gas adsorption and desorption curve are tested on Micromeritics ASAP 2020 M+C at a temperature of 150K.

SERS enhancement factor (EF) calculation.

SERS spectrum was carried out according to the literatures. The EF was calculated as follows:

$$EF = \frac{I_{SERS}}{I_{Raman}} \times \frac{N_{Raman}}{N_{SERS}}$$

Therefore:

$N_{SERS} = A_{eff}/A_{sum} \times V_{SERS} \times C_1$; $N_{Raman} = A_{eff} \times H_{eff} \times C_{sol}$.

So:

$$EF = \frac{I_{SERS}}{I_{Raman}} \times \frac{A_{eff} \times H_{eff} \times C_{sol}}{A_{eff}/A_{sum} \times V_{SERS} \times C_1}$$

$$= \frac{I_{SERS}}{I_{Raman}} \times \frac{A_{sum} \times H_{eff} \times C_{sol}}{V_{ads} \times C_1} = \frac{1.32 \times I_{SERS} \times C_{sol}}{I_{Raman} \times C_1}$$

In the above formula, N_{SERS} is the number of crystal violet molecules irradiated by laser on the SERS substrate. A_{eff} is the effective area of the laser spot. A_{sum} is the area of the SERS substrate (3 mm × 3 mm). V_{SERS} is the volume of laser irradiation (10 μL). C_1 is the concentration of crystal violet for SERS detection (g/mL). N_{Raman} is the molecular number of crystal violet in the crystal violet aqueous solution for Raman detection. H_{eff} is the effective length of the laser irradiation volume (2.2 mm). C_{sol} is the concentration of the crystal violet solution for non-SERS detection (1.077 g/mL). The peak value of SERS is 5017 (Fig. S6B) and the peak value of Raman is 1283 (Fig. S6A). The increase intensity factor of SERS substrate to 5×10^{-6} M crystal violet is 2.73×10^{6} by the above formula.

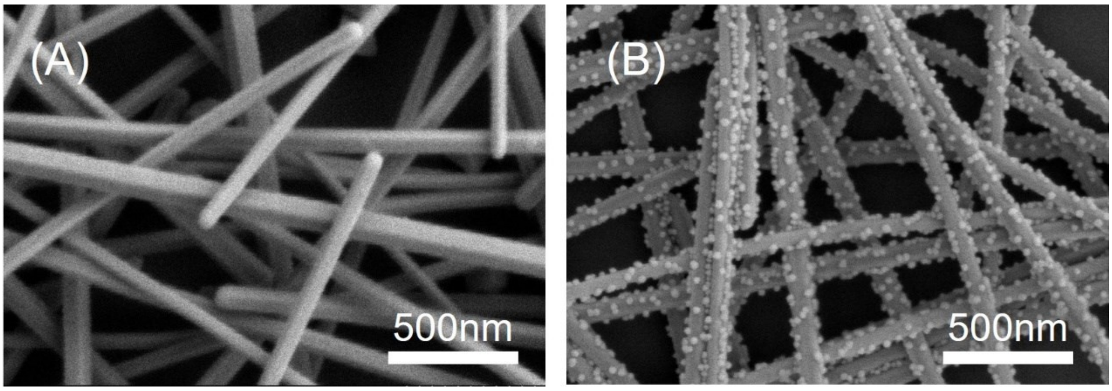


Fig. S1 (A) SEM images of the as-synthesized Ag nanowires. (B) SEM images of the Ag@Au nanowires.

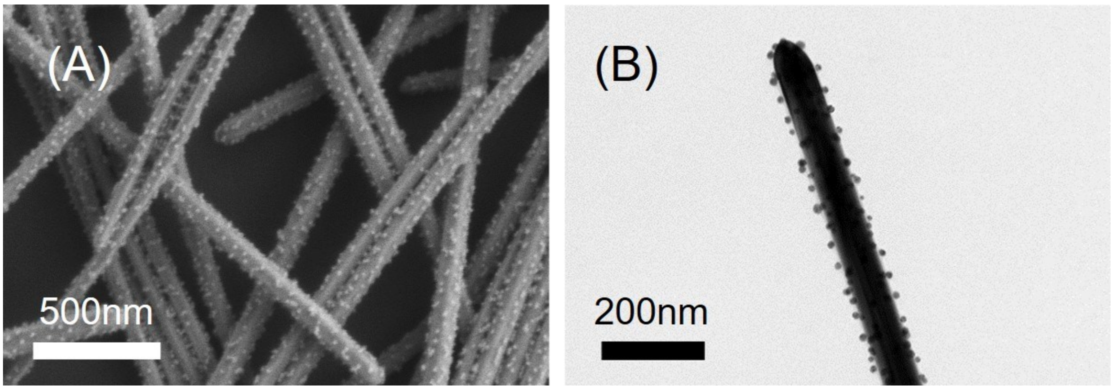


Fig. S2 (A) SEM images of the Ag@Au@ZIF-8 core/shell structure nanowires. (B) SEM images of Ag@Au@ZIF-8 core/shell structure nanowires.

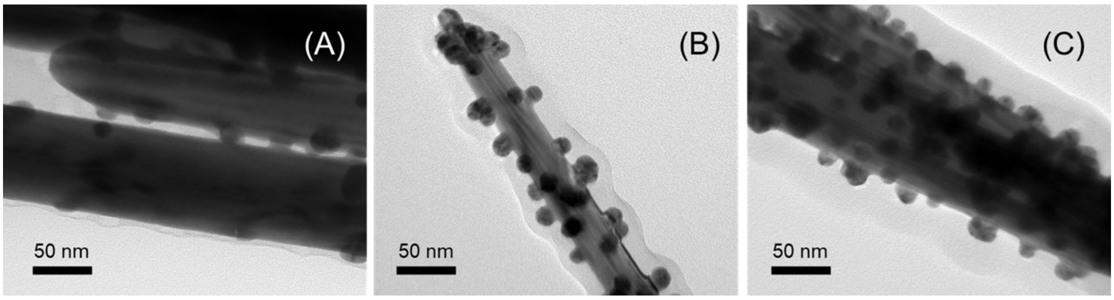


Fig. S3 (A) (B) (C) TEM images of the Ag@Au@ZIF-8 core/shell structure nanowires with different thicknesses of ZIF-8 shells (5nm, 15nm and 30nm).

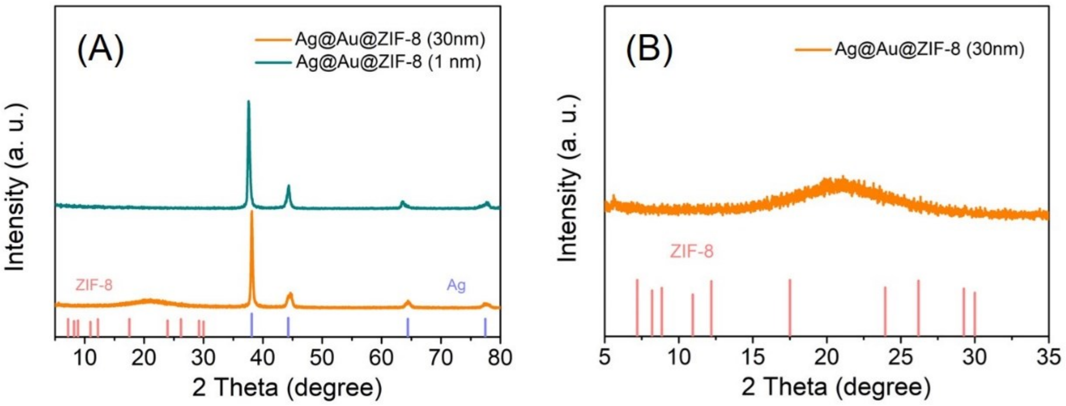


Fig. S4 (A)XRD patterns of Ag@Au@ZIF-8 nanowires. (B) Enlarged details of 5-35 degree.

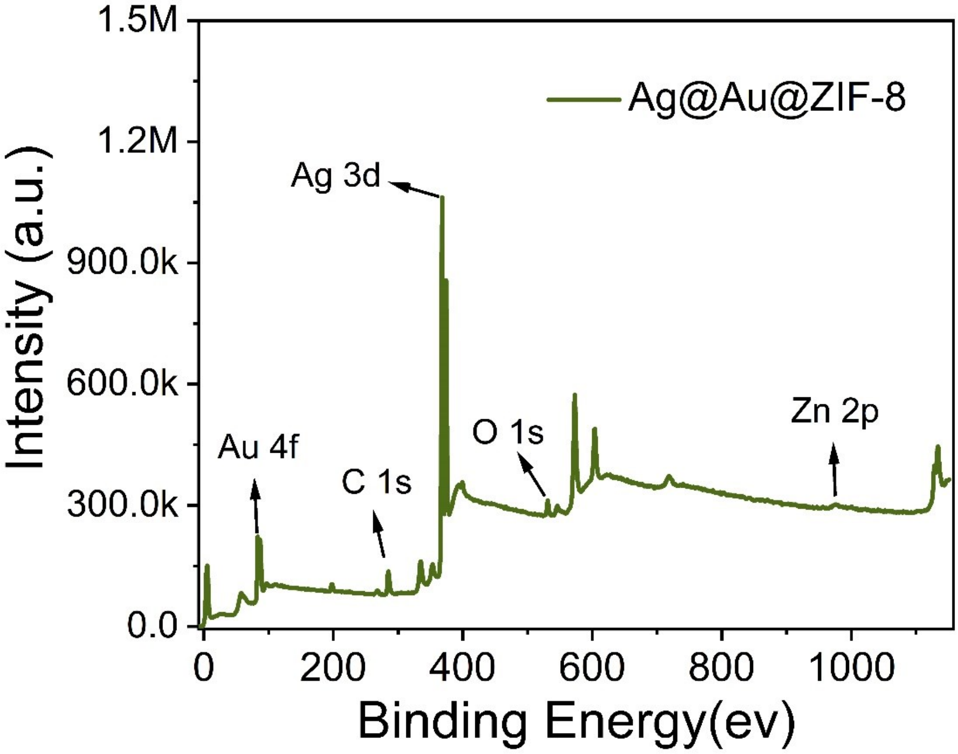


Fig. S5 XPS full-scale spectrum of Ag@Au@ZIF-8 nanowires.

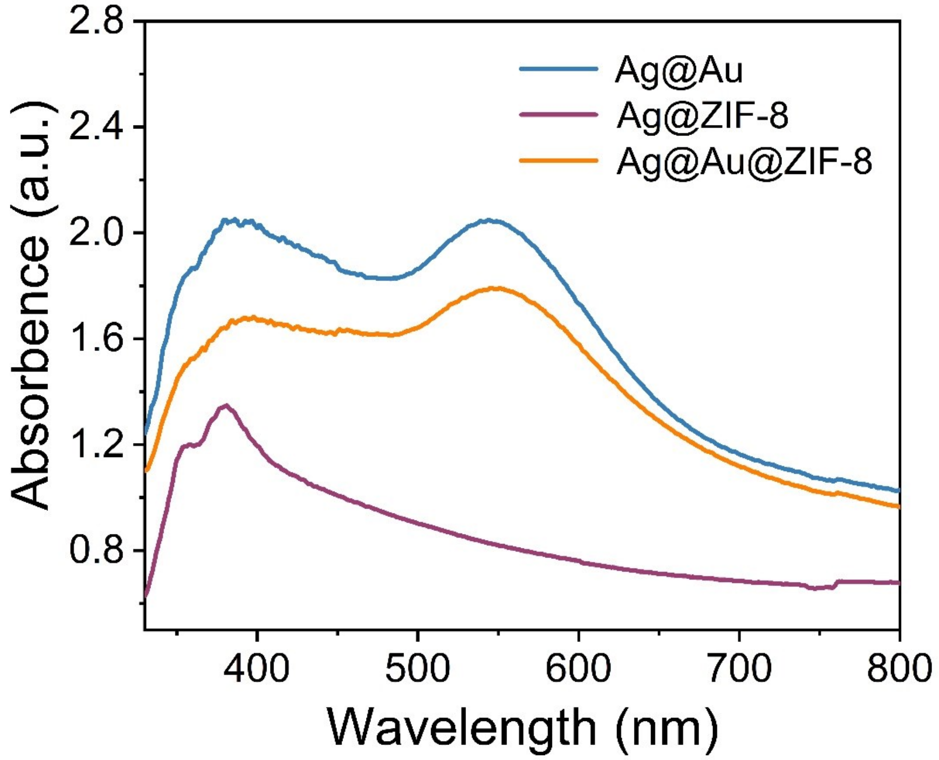


Fig. S6 UV-vis spectra of the Ag@Au nanowires, Ag@ZIF-8 nanowires and Ag@Au@ZIF-8 nanowires.

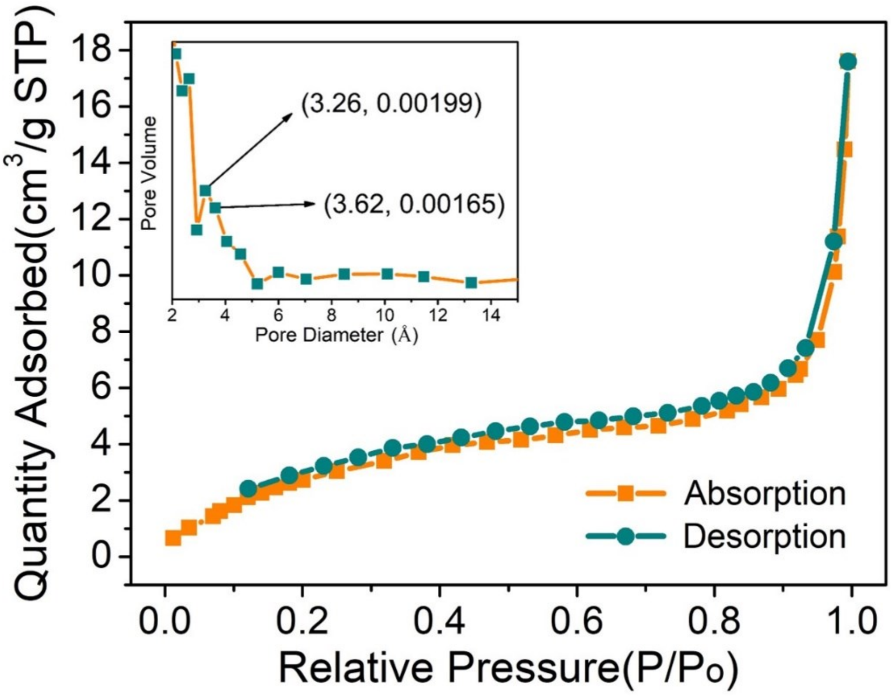


Fig. S7 Nitrogen adsorption-desorption isotherms and Insets: Pore-size distribution of the as-prepared typical Ag@Au@ZIF-8 NWs (1 nm).

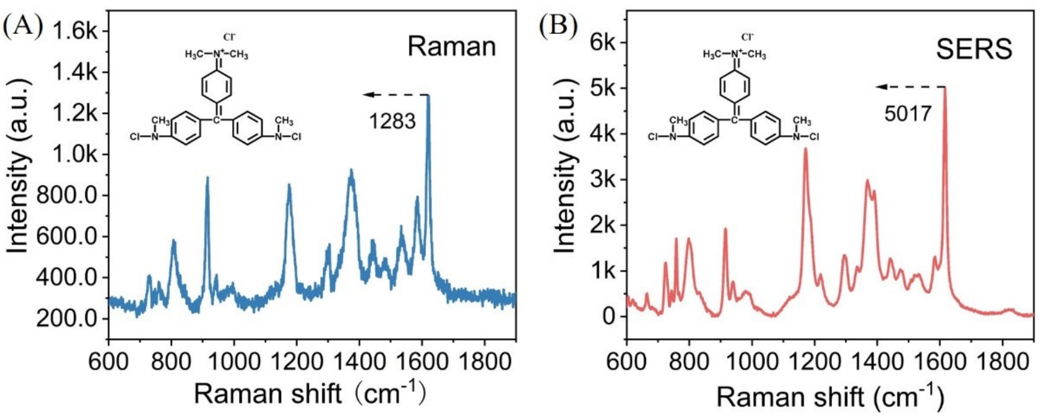


Fig. S8 (A) Raman spectrum of CV. (B) SERS spectrum of CV obtained on Ag@Au@ZIF-8 NWs/TF.

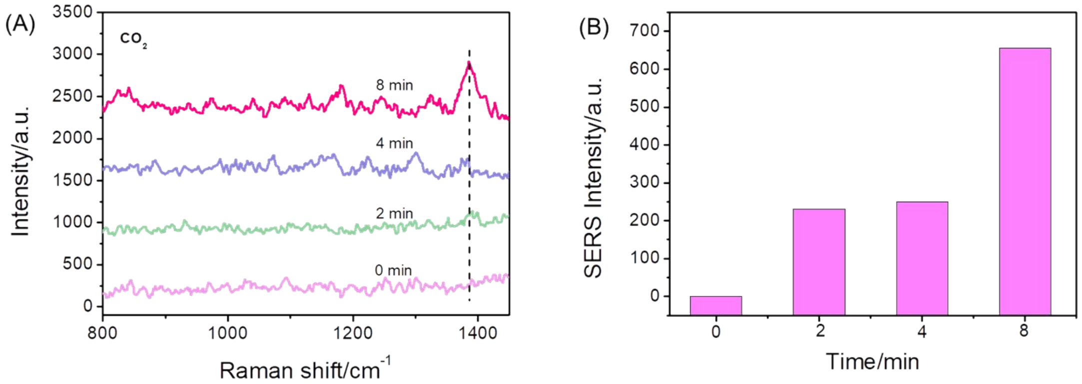
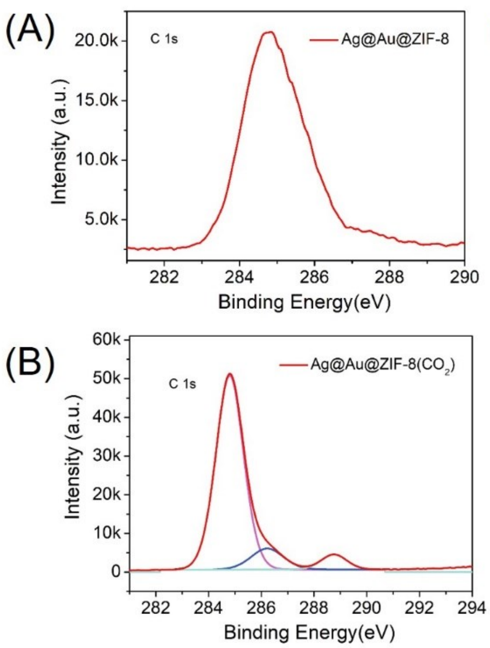


Fig. S9 (A) SERS spectrum of CO_2 gas obtained on Ag@Au@ZIF-8 NWs/TF after different time. (B) Intensity of SERS spectrum at 1395 cm^{-1} after different time.



(C)

Name	Ag@Au@ ZIF-8 Atomic %	Ag@Au@ ZIF-8 (CO$_2$) Atomic %
Au 4f	2.89	0.01
C 1s	14.69	71.12
C1 s Scan A	3.49	9.03
Ag 3d	17.21	0.06
N 1s	4.44	1.24
O 1s	4.14	13.32
Zn 2p	0.2	0.11

Fig. S10 (A) the high-resolution XPS spectra of C of Ag@Au@ZIF-8. (B) the high-resolution XPS spectra of C of Ag@Au@ZIF-8(CO$_2$). (C) Comparison table of component content of Ag@Au@ZIF-8 before and after absorption of CO$_2$ according to XPS survey spectra of the Ag@Au@ZIF-8 and Ag@Au@ZIF-8(CO$_2$).

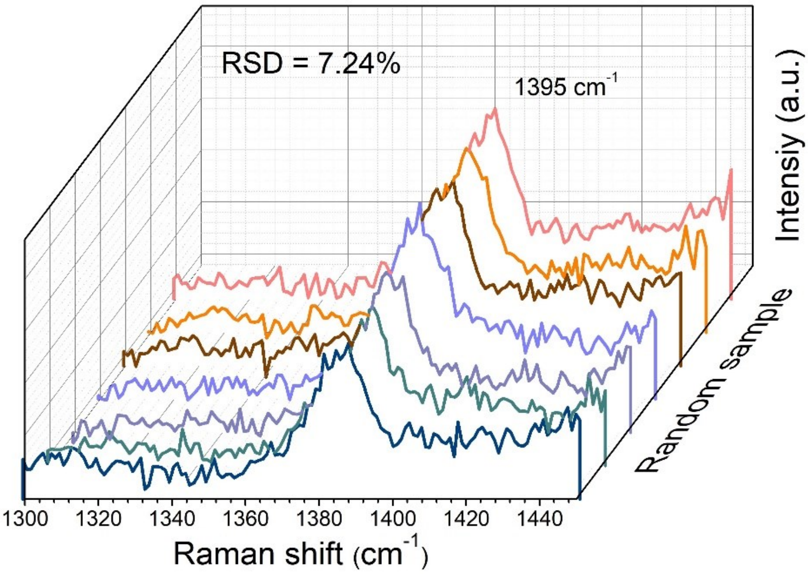


Fig. S11 SERS spectra of CO_2 collected from random sample.

Table S1 The atomic percentages of Ag@Au@ZIF-8 nanowires from XPS

Name	Atomic %
Au 4f	2.89
C 1s	14.69
C1 s Scan A	3.49
Ag 3d	17.21
N 1s	4.44
O 1s	4.14
Zn 2p	0.2

Notes and references

1. S. S. R. Dasary, A. K. Singh, D. Senapati, H. Yu and P. C. Ray, *Journal of the American Chemical Society*, 2009, **131**, 13806-13812.
2. Y. Sun, Y. Yin, B. T. Mayers, T. Herricks and Y. Xia, *Chemistry of Materials*, 2002, **14**, 4736-4745.