Supporting Information for "Facile synthesis of novel Ni-BDC-NH_2/Au NPs SERS substrates with synergistic enhancement effects for high-performance detection"

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S1. Additional experimental details

S1.1. Synthesis of Au NPs

The dynamic seed growth method was employed to synthesize Au NPs of different sizes with minor modifications[1]. Briefly, 60 mL of trisodium citrate solution (2.2 mmol/L) was heated to boiling and refluxed for 15 min. Then, 0.4 mL of $HAuCl_4$ solution (25 mmol/L) was added and the reaction was heated for 30 min. The solution changed from yellow to blue-gray, and end up with a pink gold solution. Thus, Au seed solution was prepared. After that, the seed solution was cooled down to 90℃, and 0.4 mL of $HAuCl_4$ solution (25 mmol/L) was added to the solution, stirring for 30 min, and then repeated to finish the first round of reaction. Then, 22 mL of sample solution was removed with a straw and marked as "G1". After that, the remaining sample solution was diluted with 21.2 mL of ultrapure water and 0.8 mL of sodium citrate (60 mmol/L). This resulting diluted solution served as a subsequent seed solution and the underwent the same growth process until achieving the desired generations of nanoparticles (G2-G5).

S1.2. Electrochemical measurement

The Mott-Schottky measurement was performed using an electrochemical work station (Chenhua, Shanghai) in a standard three-electrode cell. In detail, 2.0 mg of Ni-MOF powder was dispersed in 1.0 mL of ultra-pure water followed by ultrasonication for 30 min to form a homogeneous suspension. Subsequently, 20 μL of suspension was dropped onto precleaned glassy carbon electrode (1×1 cm^2) surface Finally, the

working electrodes were prepared as the glassy carbon electrode being dried. To acquire the Mott-Schottky curves, the glassy carbon electrode was immersed in a solution of 0.5 mol/L Na_2SO_4. The counter electrode used was a platinum wire, and the reference electrode was an Ag/AgCl electrode. The Mott-Schottky curves were taken at three different frequencies. The potential ranged from -0.6 to 0.8 V (vs. Ag/AgCl).

S2. Characterization of materials

S2.1 SEM images and particles size statistics of Au NPs

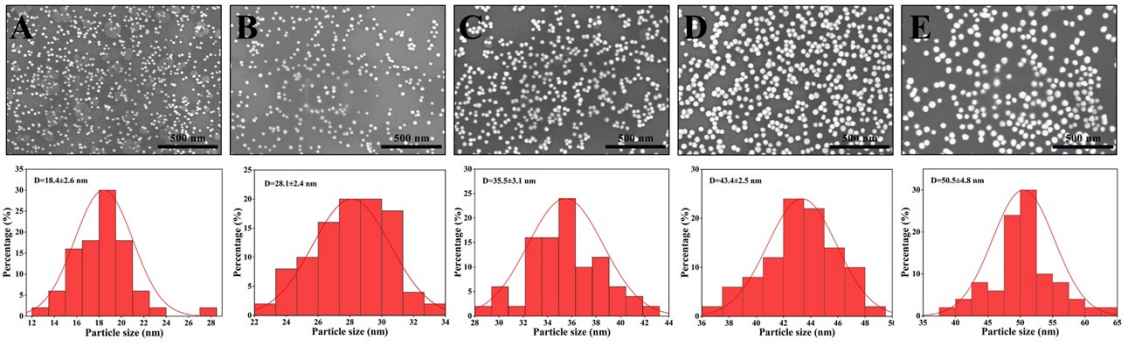

Figure S1. A-E SEM images of gold nanoparticles with different particle sizes (G1-G5) and the corresponding size distribution histograms of gold nanoparticles (n=50).

S2.2 UV-Vis of different sizes of Au NPs

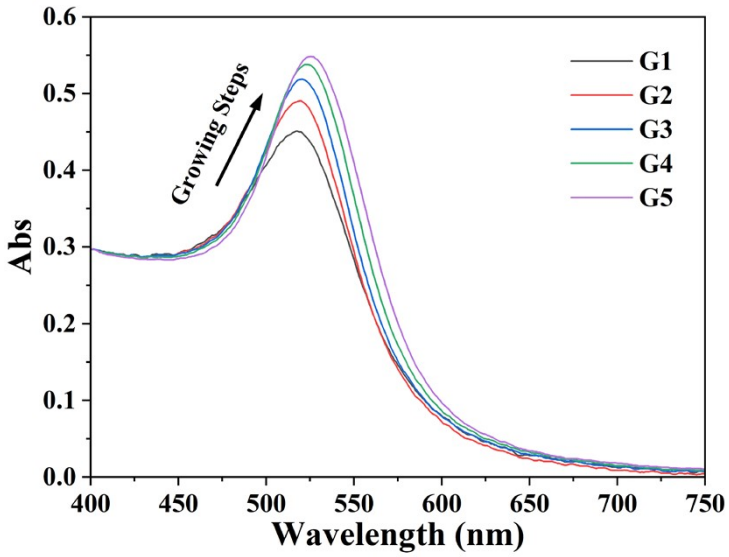

Figure S2. UV-visible absorption spectra of gold nanoparticles (G1-G5).

S2.3 N_2 adsorption and desorption curve and pore size distribution of Ni-BDC-NH_2

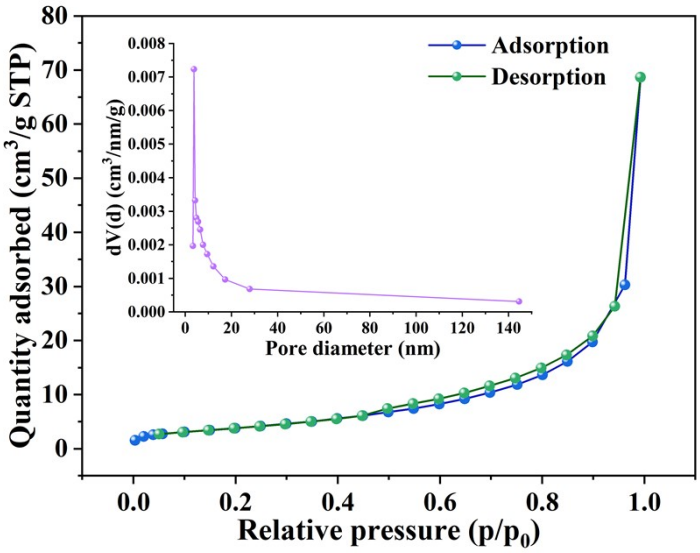

Figure S3. N_2 adsorption and desorption curve and pore size distribution map of Ni-BDC-NH_2.

S2.4 SEM image, EDS mapping images and TEM image of Ni-BDC-NH_2/Au NPs.

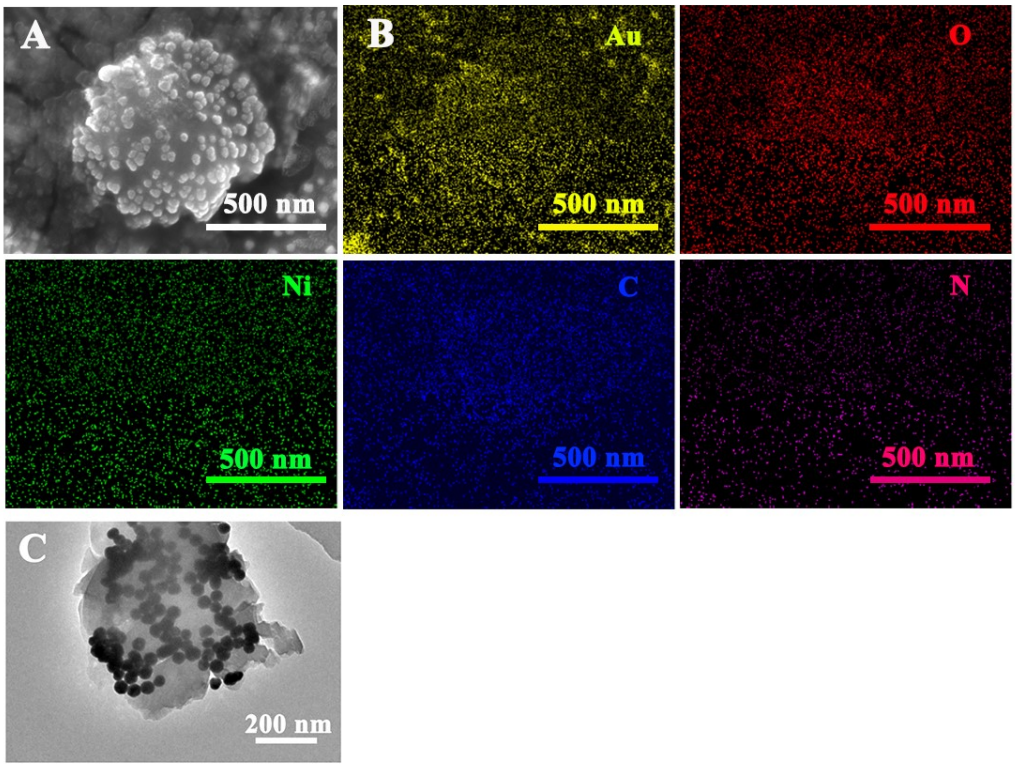

Figure S4. SEM image (A), EDS mapping images (B) and TEM image (C) of Ni-BDC-NH_2/Au NPs.

S3. Optimization of preparing conditions of Ni-BDC-NH_2/Au NPs substrate

S3.1 Effect of size of Ni-BDC-NH_2

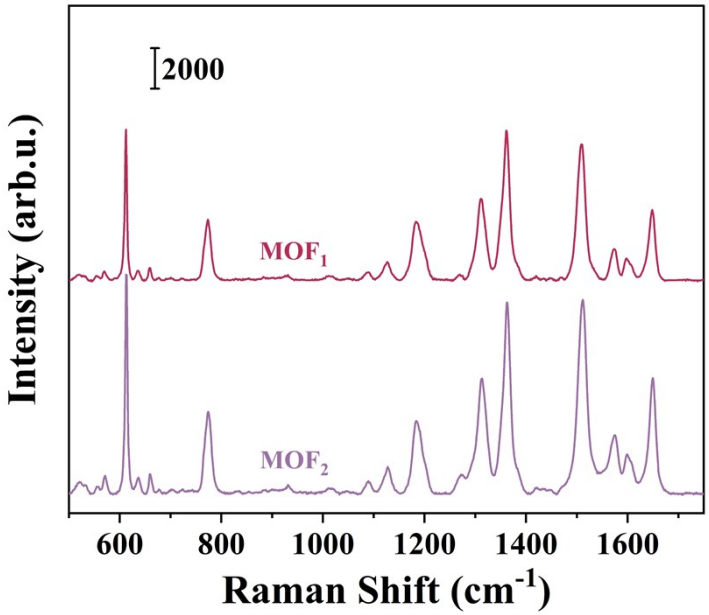

Figure S5. SERS spectra of 10^{-5} mol/L R6G on Ni-BDC-NH_2/Au NPs SERS substrates prepared by different sizes of Ni-BDC-NH_2 (MOF_1 and MOF_2).

S4. The calculation for the EF of Ni-BDC-NH_2/Au NPs SERS substrate

Enhancement factor (EF) is a significant index used for evaluating the Raman sensitivity of a SERS substrate. Here, the SERS EF value of Ni-BDC-NH_2/AuNPs substrate was calculated by utilizing the formulas based on the previous method reported[2]. The specific equation is listed as follows:

$$EF = \frac{I_{SERS} \times C_{NR}}{I_{NR} \times C_{SERS}} = \frac{4914.71 \times 0.1}{445.99 \times 10^{-7}} = 1.10 \times 10^{7}$$

Where I_{SERS} represents the SERS intensity of R6G on the Ni-MOF/Au NPs substrate, I_{NR} represents the Raman intensity of R6G. And C_{SERS} (1.0×10^{-7} mol/L) and C_{NR} (0.1 mol/L) are the corresponding concentrations of R6G used for SERS and control Raman tests, respectively. In the detection process, 20 μL of the mixed solution dripped on a glass slide. Finally, the EF value of Ni-BDC-NH_2/Au NPs substrate calculated is about 1.10×10^{7}. These results confirmed that prepared Ni-BDC-NH_2/Au NPs SERS substrate has acceptable SERS activity.

Table S1. Summary of recently reported SERS substrates used for the analysis of MB and thiram

SERS substrate	Target compounds	Linear range (mol/L)	R^2	LODs (mol/L)	Reference
CFP@PDA@Au NPs	MB	1×10^{-7}-1×10^{-3}	0.9704	1×10^{-7}	[3]
Ag ND-50	MB	1×10^{-7}-1×10^{-4}	0.998	1×10^{-7}	[4]
Fe_3O_4@SiO_2@Ag nanocomposites	thiram	1×10^{-7}-1×10^{-3}	/	1×10^{-6}	[5]
Ag dendritic nanostructures	thiram	1×10^{-7}-1×10^{-4}	/	1×10^{-7}	[6]
Ni-BDC-NH_2/Au NPs	MB	5×10^{-7}-5×10^{-5}	0.9950	5×10^{-8}	This work
	thiram	1×10^{-6}-5×10^{-4}	0.9763	5×10^{-7}	

S5. Anti-interference and selectivity test of Ni-BDC-NH_2/Au NPs SERS substrate

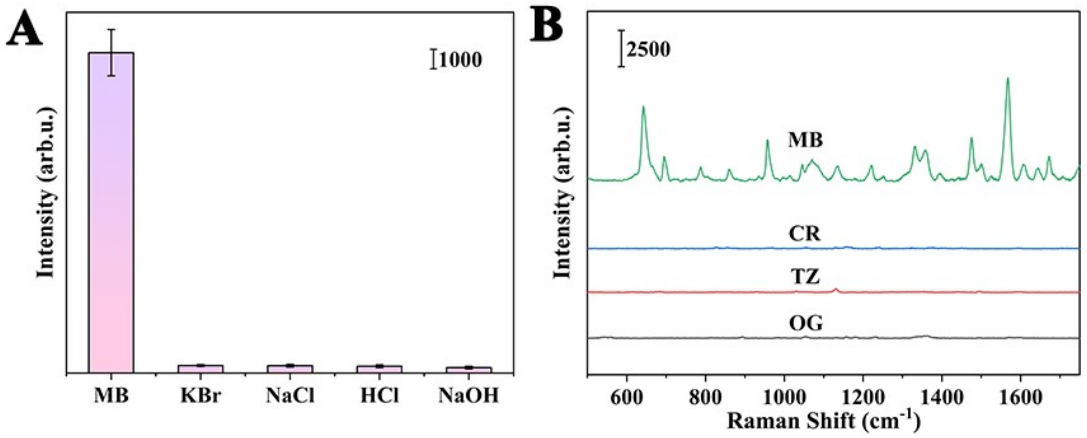

Figure S6. Anti-interference (A) and selectivity (B) of Ni-BDC-NH_2/Au NPs SERS substrates.

REFERENCES

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