Supporting Information

Stacked Hexagonal Prism of Ag@Ni-MOF-1 as Functionalized SERS Platform Through Rational Integration of Catalytic Synthesis of Dopamine-Quinone at Physiological pH with Biomimetic Route

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Contents

1. Experimental section.

Chemicals and Reagents

All chemicals and reagents used were at least of analytical grade. Ethanol, N, N-Dimethylformamide (DMF), hydrochloric acid (HCl), ascorbic acid (AA), glucose, uric acid (UA), calcium chloride ($CaCl_2$), potassium chloride (KCl), sodium chloride (NaCl) ammonium chloride (NH_4Cl) and sodium citrate (TSC) were purchased from Sinopharm Chemical Reagent Co. Ltd. Hexadecyl trimethyl ammonium bromide (CTAB), trimesic acid (H_3BTC), poly(styrene)-α-thiol-terminated (PS-SH) and 4-mercaptobenzoic acid (MBA) were obtained from Shanghai Macklin Biochemical Co. Ltd. Methylene blue (MB), silver nitrate ($AgNO_3$), Nickel chloride hexahydrate ($NiCl_2 \cdot 6H_2O$), sodium borohydride ($NaBH_4$), dopamine (DA), tyrosinase (TYR), bovine serum albumin (BSA), glutathione (GSH), gamma-glutamylcysteine (GGC), cysteine (Cys), alanine (Ala), proline (Pro), aspartic acid (Asp), homocysteine (Hcy), methionine (Met), phenylalanine (Phe) and lysine (Lys) were bought from Shanghai Aladdin Biochemical Co. Ltd. All reagents were used without further purification. Double-distilled water obtained from a Millipore water purification system (Milli-Q, 18.2 MΩ) was used in all experiments.

Synthesis of 5 nm Ag nanoparticles: 95 mL of freshly prepared aqueous solution containing $NaBH_4$ (7.5 mg) and TSC (126 mg) was heated to 60 ℃ for 30 minutes in the dark with vigorous stirring. After that, 5 mL of $AgNO_3$ (20 mg) solution was added to the mixture. Then, the temperature was further raised to 90 ℃ and the pH of the solution was adjusted to 10.5 using 0.1 M NaOH aqueous solution. Heating was continued for 20 minutes to get the 5 nm Ag nanoparticles. In order to remove the unreacted reductants, Ag nanoparticle suspensions were centrifuged (12000 rpm, 15 min) and washed thrice, followed by re-dispersion in water and were stored at 4 ℃ for future use.[S1]

Synthesis of Ni-MOF-1

Ni-MOF-1 was synthesized by our new method. 12 mL of DMF solution containing $NiCl_2 \cdot 6H_2O$ (1.427 g, 6 mmol), CTAB (2 g, 5 mmol) and H_3BTC (1.05 g, 5 mmol) was added in a Teflon reaction vessel and was adjusted pH with 0.1 mL 10% concentrated HCl. After 10 minutes sonication, the reactor was placed inside an oven at 120 °C for 48 h. After heating, light green solution was obtained

and centrifugal washed three times by DMF and ethanol respectively (12000 rpm, 15 minutes). Finally, the washed light green solid was dried overnight in vacuum to get the Ni-MOF-1.

Synthesis of Ag@Ni-MOF-1

Ag@Ni-MOF-1 was synthesized by a little modifications to the synthesis method of Ni-MOF-1. A certain amount of silver nanoparticles need to be added in the Teflon reaction vessel before sonication. Subsequent processing steps were the same as above.

Prepared of the SERS probe (Ag@Ni-MOF-1/DA-quinone)

First, Ag@Ni-MOF-1 was immerged in DA solution (0.01 mM) at pH 4.0 for 6 hours, facilitating uniform distributions of the DA on the Ag particle surfaces to form Ag@Ni-MOF-1/DA. Then, Ag@Ni-MOF-1/DA was centrifugally (6000 rpm, 5 min) washed with water and anhydrous ethanol three times. Secondly, Ag@Ni-MOF-1/DA was added into the PBS solution (pH 7.4) for 10 min to form Ag@Ni-MOF-1/DA-quinone for SERS measurements of Cys.

In vivo microdialysis

All procedures involving animals were conducted with approval of the Animal Ethics Committee in East China Normal University, China. Normal and APPswe/PS1dE9 transgenic mouse model of AD (25-30 g) was purchased from Shanghai Biomodel Organism Science & Technology Development Co. Ltd (Shanghai, China). The age at the time of recording was 5-6 months. Surgeries for in vivo microdialysis were performed as reported previously.[S2] The microdialysis probe (CMA7 Tub) was implanted in the striatum at the site of 0.5 mm anterior to bregma, 2.0 mm lateral from midline, and 3.0 mm below dura. Throughout the surgery, the body temperature of the animals was maintained at 37 °C with a homoeothermic blanket (Beijing Tide-Gene Biotechnology Development Center). The microdialysis probes (CMA7 Tub) were implanted into the striatum of mouse and were perfused with a CSF solution at 2 $\mu L \cdot min^{-1}$ for at least 90 min for equilibration. After that, 200 μL of brain dialysates were collected for SERS measurements.

Determination of Cys in brain dialysate.

The SERS spectra of Ag@Ni-MOF-1/DA-quinone was initially obtained in a cell (1 mL) filled with aCSF solution with pH 7.4 (200 μL). Meanwhile, the brain microdialysate (200 μL) was collected from the mouse brain by microdialysis probe. Then, the aCSF solution was removed and 200 μL brain microdialysate was immediately added into the cell. The detection Cys concentration was determined after Ag@Ni-MOF-1/DA-quinone was reacted with Cys in brain microdialysate for 10 min.

Apparatus and Measurements

Transmission electron microscopy (TEM) images were performed on FEI Tecnai G2 F30 instrument (FEI, Netherlands). Scanning electron microscopy (SEM) images were recorded on S-4800 SEM instrument (Hitachi, Japan). Power X-ray diffraction (PXRD) were carried out on a Rigaku Ultima IV X-ray diffractometer with Cu Kα radiation. XPS characterization was performed on a PHI-5000ESCA system (Perkin Elmer). All pH measurements were performed using a pH-3c digital pH meter (Shanghai Lei Ci Device Works, Shanghai, China) with a combined glass-calomel electrode. Nitrogen adsorption-desorption isotherm was collected on Autosorb iQ2 at 77 K. Pore size distribution of the materials were derived from the Horvath-Kawazoe (HK) model using the adsorption branch on the isotherm. Raman spectra were performed on Renishaw inVia Raman Microscope in the range of 760~1760 cm^{-1}. A 532 nm laser was used for all the measurements. For SERS measurements of solution samples, a 10× (NA 0.5) microscope objective with a working distance of 10.6 mm and a spot-focused laser were used. The laser power and acquisition time were 10 mW and 1 s, respectively. The obtained SERS spectra were first processed by carrying baseline correction and smoothing to remove the background and noise.

Density function theory (DFT) method

All the calculations was performed within the framework of the density functional theory (DFT) as implemented in the Vienna Ab initio Software Package (VASP 5.3.5) code within the Perdew–Burke–Ernzerhof (PBE) generalized gradient approximation and the projected augmented wave (PAW) method.[S2-S5] The cutoff energy for the plane-wave basis set was set to 400 eV. The Brillouin zone of the surface unit cell was sampled by Monkhorst–Pack (MP) grids, with a Γ k-point mesh for Ag(111) structure optimizations.[S6] The convergence criterion for the electronic self-

consistent iteration and force was set to 10^{-5} eV and 0.01 eV/Å, respectively. The climbing image nudged elastic band (CI-NEB) [S7-S9] method was used to confirm the transition states with only one imaginary frequency along the reaction coordinates. A 5×5 supercell of the Ag(111) surface including 4 atomic layers was constructed to model the Fe catalyst in this work, with the bottom two layers fixed in structural relaxation. A vacuum layer of 12 Å was introduced to avoid interactions between periodic images. The adsorption energy (E_{ads}) of the surface species is defined by $E_{ads} = E_{total} - E_{surface} - E_{species}$,

where E_{total} represents the total energy of the adsorbed species with catalyst surface, $E_{surface}$ is the energy of the empty surface, and $E_{species}$ is the energy of the species in the gas phase.

2. Characterization of AgNPs.

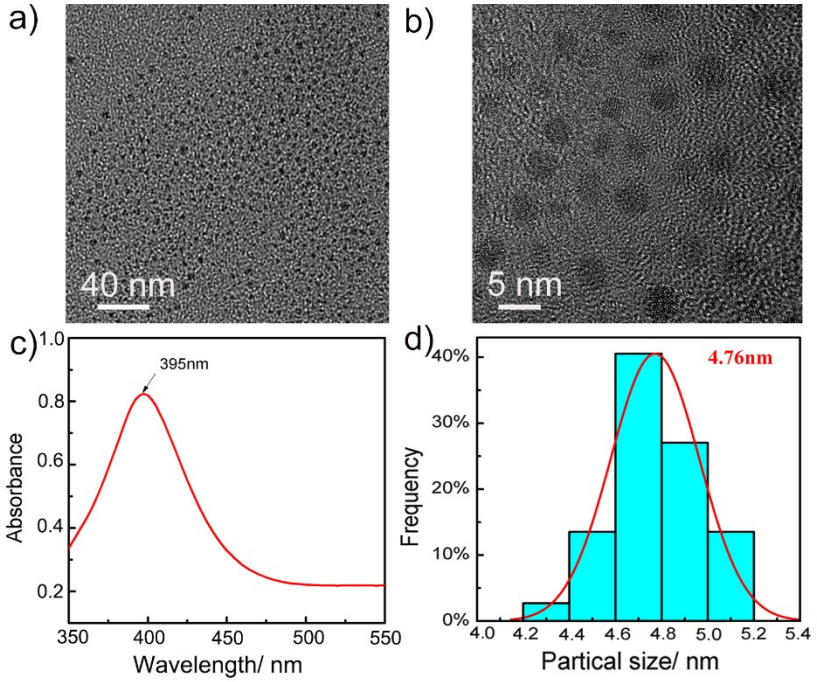

Fig. S1 (a-b) TEM image, (c) UV-Vis spectrum, and (d) size distribution of AgNPs.

3. SEM and TEM images of Ni-MOF-1.

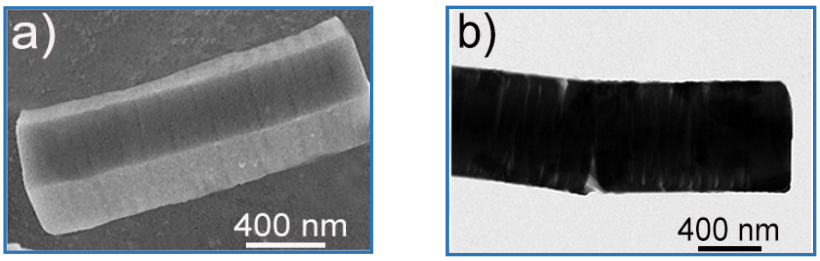

Fig. S2 a) SEM and b) TEM images of Ni-MOF-1.

4. HRTEM of AgNPs in Ag@Ni-MOF-1

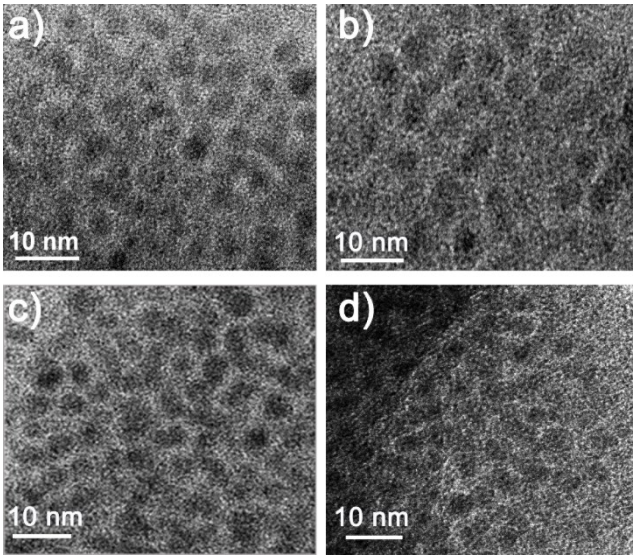

Fig. S3 HRTEM of AgNPs in Ag@Ni-MOF-1

5. EDX result of Ag@Ni-MOF-1.

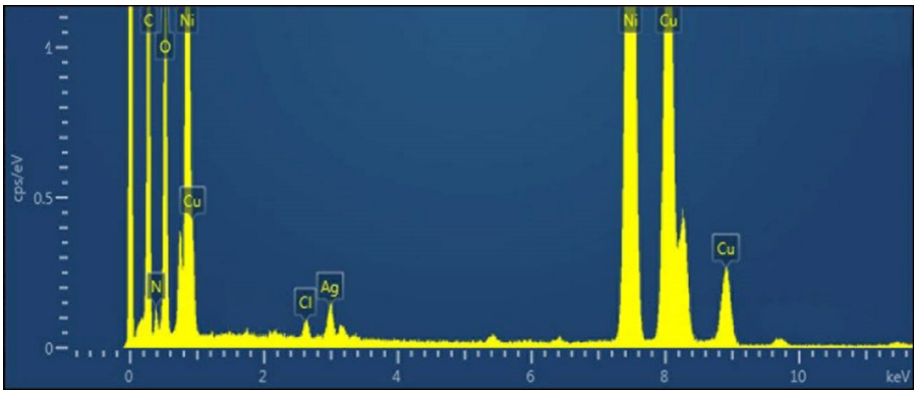

Fig. S4 EDX result of Ag@Ni-MOF-1.

6. XRD spectra of Ag@Ni-MOF-1

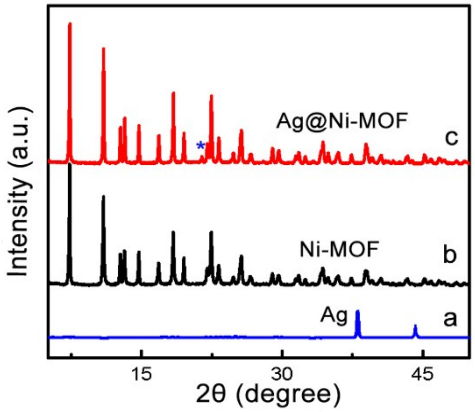

Fig. S5 XRD patterns of a) Ag, b) Ni-MOF-1 and c) Ag@Ni-MOF-1.

7. Molecular sieve effect of Ag@Ni-MOF-1

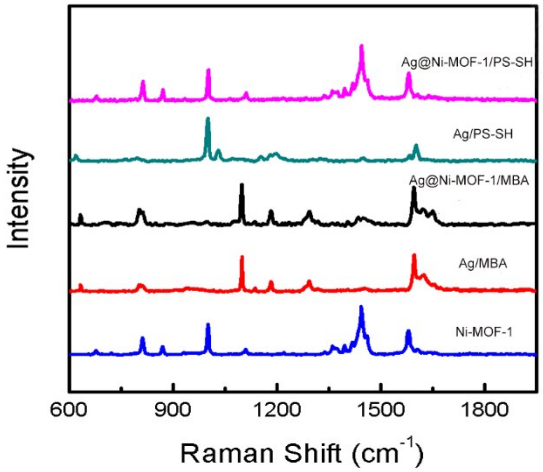

Fig. S6 SERS spectra of Ag@Ni-MOF-1 and AgNPs incubation with MBA or PS-SH.

8. High-resolution XPS spectra of Ag@Ni-MOF-1

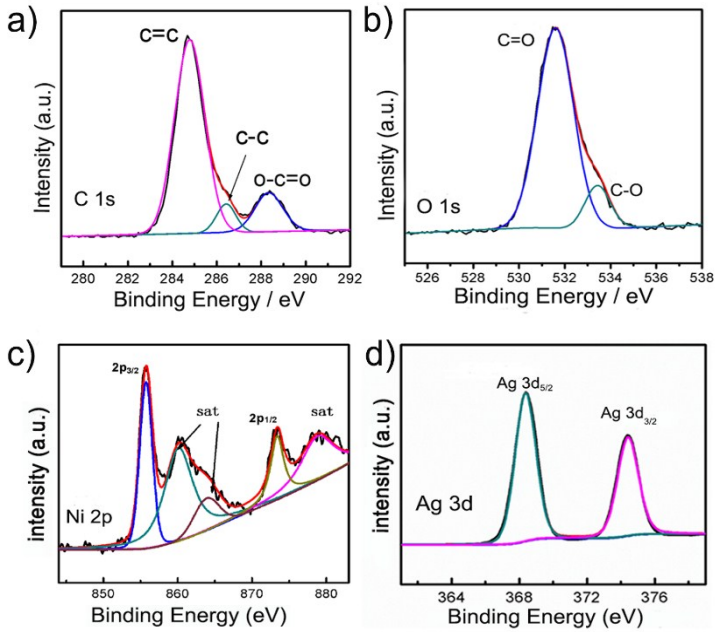

Fig. S7 XPS spectra of a) C 1s; b) O 1s; c) Ni 2p; d) Ag 3d of Ag@Ni-MOF-1.

9. N_2 adsorption-desorption isotherms of Ag@Ni-MOF-1

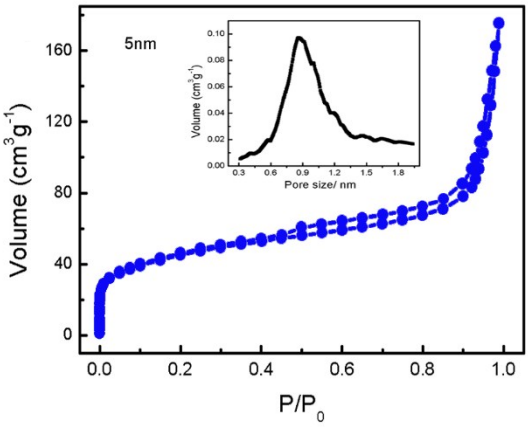

Fig. S8 N_2 adsorption-desorption isotherms of Ag@Ni-MOF-1. Inset: the Horvath-Kawazoe (HK) model pore size distribution calculated from the adsorption branch of the isotherm.

10. Calculation of SERS enhancement factors (EFs) of 5 nm Ag and Ag@Ni-MOF-1.

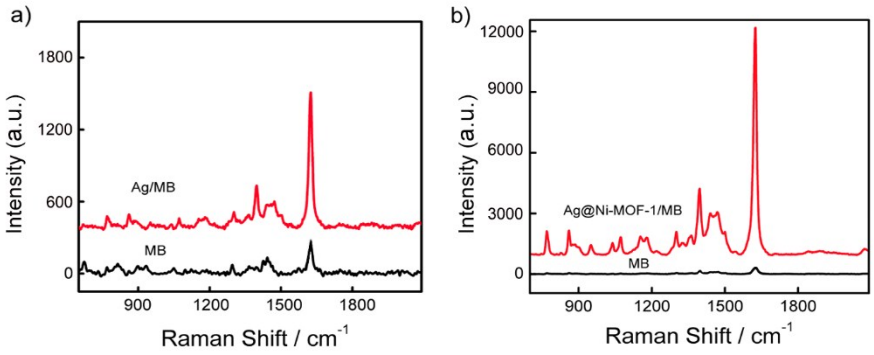

Fig. S9 a) The normal Raman spectra of pure methylene blue (MB) solution (10 mM) and SERS spectra of 100 μM MB at the surface of 5 nm AgNPs. b) Raman spectra of pure MB solution (10 mM) and 1 μM MB in Ag@Ni-MOF-1. The measured SERS spectra were obtained by taking the average of 10 measurements.

From the Fig. S8, we could calculate I_{SERS} and I_{bulk}.

I_{SERS} = 10907.7 (Ag@Ni-MOF-1); I_{SERS} = 1186.3 (Ag); I_{bulk} = 335.8 (based on the peak of 1623 cm^{-1}).

N_{ads} and N_{bulk} represent the number of MB molecules in the SERS sample and the normal Raman sample, respectively. I_{SERS} and I_{bulk} are the same vibration peak of MB molecule on one Ag and the normal Raman spectrum from solid sample, respectively.

According to the enhancement factor (EF) = (I_{SERS} / N_{ads}) / (I_{bulk} / N_{bulk})

The EFs of 5 nm Ag and Ag@Ni-MOF-1 were following:

Materials	EF
5 nm AgNPs	1.17×10^4
Ag@Ni-MOF-1	3.26×10^7

11. SERS spectra of Ag@Ni-MOF-1/DA at different pH

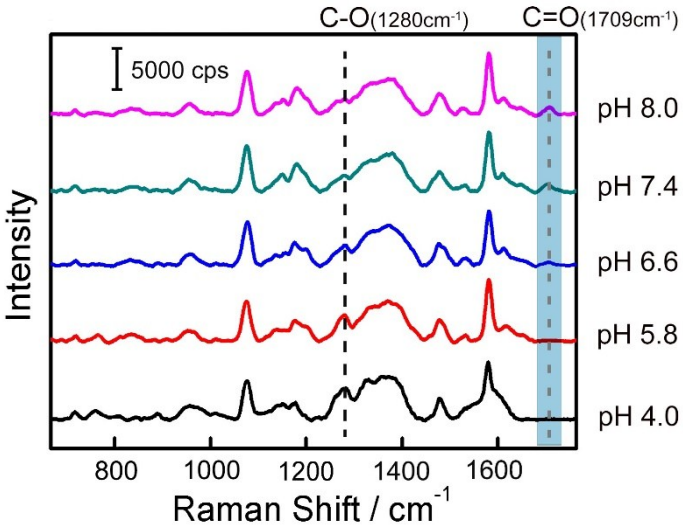

Fig. S10 SERS spectra of Ag@Ni-MOF-1/DA under different pH.

12. Effect of DA concentrations on conversion ratio

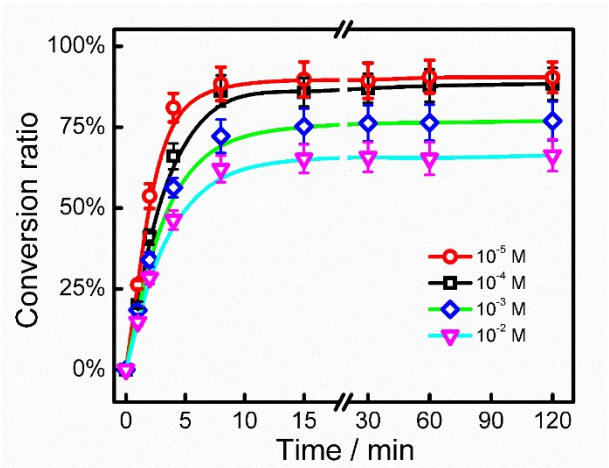

Fig. S11 Effect of different DA concentrations on its conversion ratio in Ag@Ni-MOF-1.

13. Molecular size calculation and selectivity

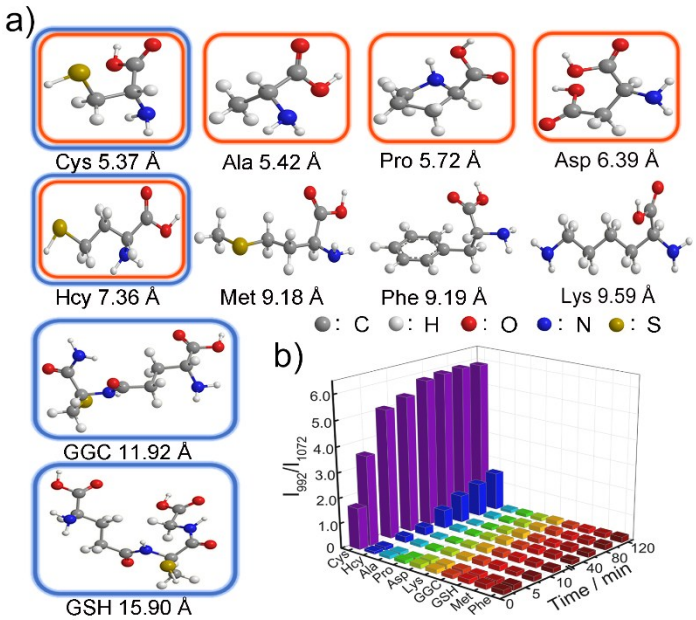

Fig. S12 a) The structure and molecular size of typical amino acids and molecules with sulfhydryl existing in mouse brain. b) The selectivity test of typical amino acids and molecules with sulfhydryl against Cys. The red frame represents the molecule with size smaller 0.86 nm, the blue one is the molecule containing sulfhydryl groups.

14. Selectivity and competition tests.

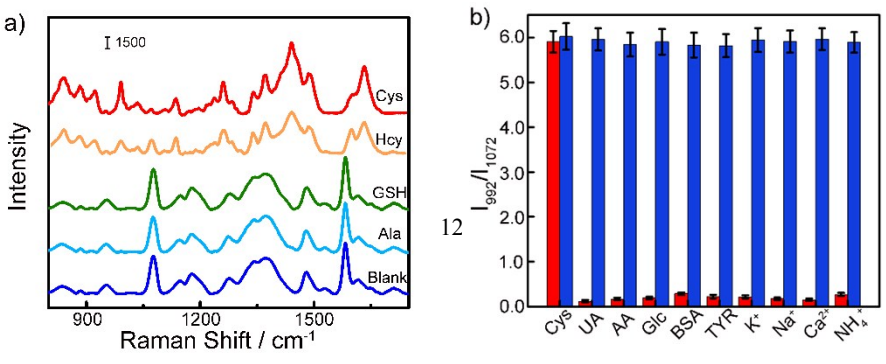

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Fig. S13 a) Typical SERS spectra of Ag@Ni-MOF-1/DA-quinone in the absence and presence of different interferences. b) Selectivity (red column) and competition (blue column) tests of interferences against Cys: AA (100 μM), UA (100 μM), glucose (5 mM), BSA (0.5 mg/mL), TYR (0.5 mg/mL), K^+ (1 mM), Na^+ (1 mM), Ca^{2+} (100 μM), NH_4^+ (100 μM). Error bars represent standard deviation.

15. SERS spectra of some amino acid with Ag@Ni-MOF-1 without DA-quinone.

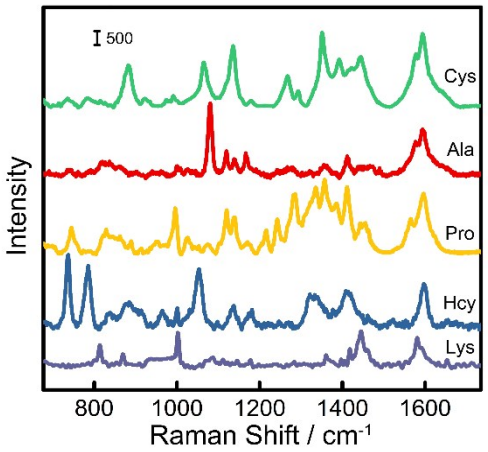

Fig. S14 SERS spectra of Cys, Ala, Pro, Hcy and Lys with Ag@Ni-MOF-1 without DA-quinone.

The concentrations of all molecules used here were all 0.1 mM,

16. SERS bands assignment

Table S1. SERS bands assignment of DA-quinone (Figure S8) before and after reaction with Cys (Figure 5a).

DA-quinone		DA-quinone + Cys (5-Cys-DA)	
Shift /cm^{-1}	Assignment	Shift /cm^{-1}	Assignment
833	C-H bending C-N stretching	838	C-H bending C-N stretching
959	C-H non-symmetric	885	COO^- stretching

			C-COO^- stretching
1076	C-C stretching C–H in-plane bending	924	COO^- stretching
1147	C-C stretching	992	Ring breathing
1177	C-H bending C-C stretching C-H scissoring	1032	C-N stretching
1280	C-O stretching	1072	C-C stretching C–H in-plane bending
1341	C-H bending	1137	C-C stretching
1370	Ring stretching	1260	C-N stretching
1480	C-C stretching C-H scissoring	1283	C-O stretching
1580	Ring stretching	1341	C-H bending
1617	C=C stretching	1370	Ring stretching
1709	C=O stretching	1441	C-H bending C-H scissoring COO- stretching
		1480	C-C stretching C-H scissoring
		1600	Ring stretching
		1635	C=N stretching C=C stretching

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