

**A simple prepared SERS sensor based on antibody-modified
 $\text{Fe}_3\text{O}_4@Au$ MNPs for the detection of CA19-9 in CRC patients**

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1. Interference evaluation

The SERS spectra was detected after mixing the CA19-9 solution (10 U/mL) separately with the CEA and CA125 solutions (both at 1000 U/mL). Fig. S1 showed that the ratio of the characteristic peak I_{1392}/I_{1069} remained unchanged. It indicated that CA19-9 detection by the SERS sensor without interference from other substances in serum.

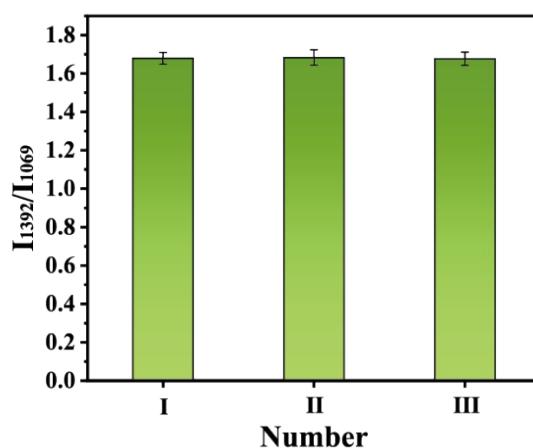


Fig. S1 SERS spectra of CA19-9 solution (10 U/mL) mixed with CEA and CA125 solution (both at 1000 U/mL) respectively. (I) 10 U/mL CA19-9 solution; (II) 10 U/mL CA19-9 solution + 1000 U/mL CEA solution; (III) 10 U/mL CA19-9 solution + 1000 U/mL CA125 solution

2. SERS detection

Different concentrations of CA19-9 antigen (0.01, 0.1, 1, 10, 100 and 1000 U/mL) were detected by SERS sensor. Fig. S2 showed the local amplification of the SERS spectra obtained, which could see the change of characteristic peak more clearly.

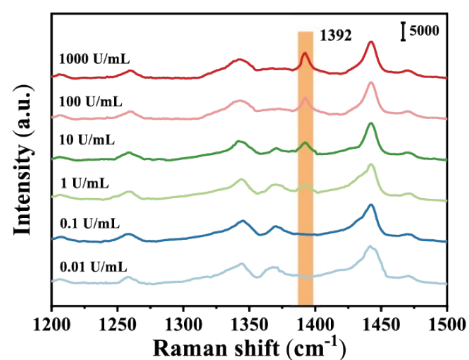


Fig. S2 SERS spectra obtained from the reaction of SERS sensor with CA19-9 antigen of different concentrations (0.01, 0.1, 1, 10, 100 and 1000 U/mL)

3. Clinical sample Analysis

The CA19-9 concentrations in serum samples from 30 healthy individuals and 30 CRC patients were shown in Table S1 and Table S2.

Table S1 Results of the SERS sensor for health individuals

Sample	CA19-9 (U/mL)
1	10.702
2	8.667
3	11.988
4	6.462
5	7.803
6	13.848
7	14.782
8	11.422
9	5.613
10	6.891
11	18.373
12	26.605
13	9.569
14	8.202
15	12.371
16	9.089
17	7.003
18	13.988
19	16.726
20	14.067
21	13.270
22	12.495
23	7.629
24	22.387
25	19.118
26	16.930
27	9.479
28	13.603
29	8.866
30	12.990

Table S2 Results of the SERS sensor for CRC patients

Sample	CA19-9 (U/mL)
1	48.318
2	67.497
3	61.907
4	52.749
5	70.225
6	39.750
7	49.411
8	54.264
9	42.752
10	56.778
11	68.014
12	38.401
13	47.433
14	72.362
15	42.445
16	62.371
17	92.032
18	51.319
19	71.831
20	59.086
21	41.990
22	43.257
23	45.062
24	64.405
25	52.531
26	59.820
27	40.004
28	79.521
29	83.297
30	57.564