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SERS Hotspot Engineering Using External Field Assembly of Plasmonic Magnetic Nanocomposite with High Sensitive and UniformityZhenli Sun[a], Ning Wang[a], Yiyan Zhang[a], Xunlong Ji [a], Zijin Hong[a], Dan Xie[a], Wentao Zhang[a], Wenjing Liu[b], Jingjing Du[c,d*]

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4-MPY Density calculations:

1 Calculation of hot spot density

① There are 30 mg $Fe_3O_4@SiO_2$（FS） nanoparticle in 3 mL water, the number of FS was

$$N_{FS}=\frac{m_{FS}}{M_{FS}}=\frac{30\times 10^{-3}}{2.2\times\frac{4\pi}{3}\left((153\times 10^{-7})^3-(150\times 10^{-7})^3\right)+5.18\times\frac{4\pi}{3}(150\times 10^{-7})^3}$$

$=4.0\times 10^{11}$

② Take 0.5 mL of FS substrate, remove the supernatant, and add 0.25 mL of de-ionized water, the amount of FS

$$N_{FS'}=\frac{0.5}{3.0}\times N_{FS}=\frac{0.5}{3.0}\times 4.0\times 10^{11}=6.7\times 10^{10}$$

③ The number of 4 μL substrate nanoparticle used for SERS detection was

$$N_{FS0}=6.67\times 10^{10}\times\frac{4\times 10^{-3}}{3}=8.9\times 10^{7}$$

④ The distribution area of FA particles was 8.66 mm^2 (Figure S 2a) before enrichment of the substrate with the magnet and 1.34 mm^2 (Figure S 2g) in the presence of the magnet, respectively, and thus the density of FA particles before and after enrichment was

Before enrichment: $D_{FS1} = \frac{8.9 \times 10^7}{8.66} = 1.0 \times 10^7\, per\, mm^2$

After enrichment: $D_{FS2} = \frac{8.9 \times 10^7}{1.34} = 6.6 \times 10^7\, per\, mm^2$

⑤ Calculation of FA particle gap before and after enrichment (gap)

Before enrichment: $G_{FA1} = \frac{1}{\sqrt{1.0 \times 10^7}} = 0.31\, \mu m$

After enrichment: $G_{FA2} = \frac{1}{\sqrt{6.6 \times 10^7}} = 0.12\, \mu m$

⑥ Calculation of density of hot spots before and after enrichment（density of hot spots, D_{HS}）

Before enrichment:

$D_{HS1} = 2 \times \sqrt{1.0 \times 10^7} \times \left(\sqrt{1.0 \times 10^7} + 1\right) = 2.1 \times 10^7\, per\, mm^2$

After enrichment:

$D_{HS2} = 2 \times \sqrt{6.6 \times 10^7} \times \left(\sqrt{6.6 \times 10^7} + 1\right) = 1.3 \times 10^8\, per\, mm^2$

2 Calculation of Density calculation for FA surface 4MPY

① Based on the results of the SERS detection (Figure S 1), the amount of 4MPY adsorbed on the 4 μL FA substrate was

$N_{AM} = C_{4MPY} \times V_{4MPY} = (10.0 - 0.15) \times 10^{-6} \times 1 \times 10^{-3} \times 6.02 \times 10^{23} = 5.93 \times 10^{15}$

② The number of 4MPY on each FA particle is:

$N_{4MPY0} = \frac{5.93 \times 10^{15}}{8.9 \times 10^7} = 6.7 \times 10^7$

③ Before and after enrichment, the density of AM distribution was（density of AM, D_{AM}）

Before enrichment:

$D_{4MPY1} = 6.7 \times 10^7 \times 1.0 \times 10^7 = 6.9 \times 10^{14}\, per\, mm^2$

After enrichment:

$D_{4MPY2} = 6.7 \times 10^7 \times 6.6 \times 10^7 = 4.5 \times 10^{15}\, per\, mm^2$

④ Per FA surface, 4 MPY density distribution was

Based on previously studies, the spacing of gold nanoparticles on the FA surface is 7 nm, so the number of gold nanoparticles per FA surface was

$$N_{Au}=\frac{4\pi\times\left(R+r+\frac{space}{2}\right)^2}{\pi\times\left(r+\frac{space}{2}\right)^2}=\frac{4\pi\times\left(155+10+\frac{7}{2}\right)^2}{\pi\times\left(10+\frac{7}{2}\right)^2}=587$$

The surface area of per FA particle was

$$S_{FA}=S_{FA}+S_{Au}\times N_{Au}=4\pi R^2+4\pi r^2\times 587=4\pi 155^2+4\pi 10^2\times 587=1.08\times 10^6$$

The density distribution of 4MPY on the FA surface was

$$D_{AM3}=\frac{N_{4MPY0}}{S_{FA}}=\frac{6.7\times 10^7}{1.08\times 10^6}=62\ per\ nm^2$$

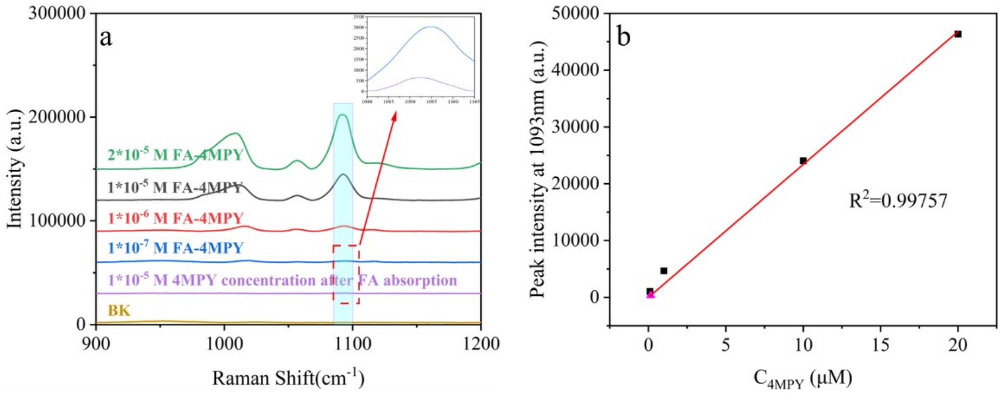

Figure S 1 (a)Signal intensity plots of Raman spectra of 4MPY at different dilutions (b) The calibration curve of 4MPY (the inserted red-purple point was 4MPY concentration after FA absorption.).

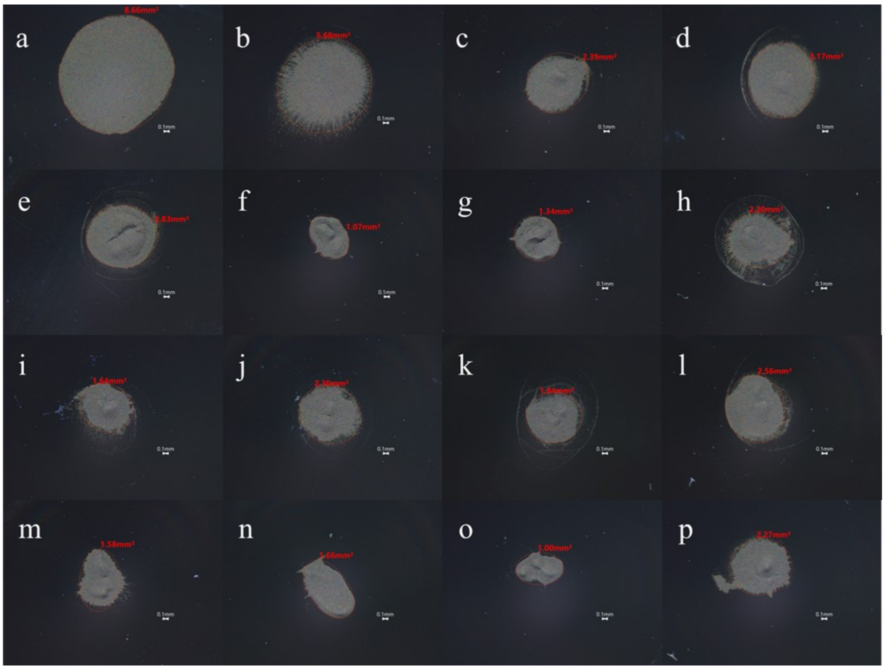

Figure S 2 White light map of magnetic FA particle distribution after enrichment with different magnets.

Table S 1 Effect of different magnet sizes on the substrate

Sample	Magnetic fields (mT)	Diameter of magnet (mm)	Thickness of magnet (mm)	Area (mm^2)	GAP (μm)	density of hot spots (per mm^2)	density of AM (per mm^2)
a	0	0	0	8.66	0.31	2.1E+07	6.9E+14
b	22	1	1	5.68	0.25	3.1E+07	1.0E+15
c	26	1	2	2.39	0.16	7.4E+07	2.5E+15
d	67	2	1	3.17	0.19	5.6E+07	1.9E+15
e	87	2	2	2.83	0.18	6.3E+07	2.1E+15
f	96	3	1	1.07	0.11	1.7E+08	5.6E+15
g	103	3	2	1.34	0.12	1.3E+08	4.5E+15
h	126	3	3	2.20	0.16	8.1E+07	2.7E+15
i	138	3	4	1.64	0.14	1.1E+08	3.6E+15
j	143	3	5	2.30	0.16	7.7E+07	2.6E+15
k	144	3	6	1.84	0.14	9.7E+07	3.2E+15
l	113	4	1	2.56	0.17	7.0E+07	2.3E+15
m	170	4	2	1.58	0.13	1.1E+08	3.8E+15
n	102	5	1	1.66	0.14	1.1E+08	3.6E+15
o	187	5	2	1.00	0.11	1.8E+08	6.0E+15
p	185	7	2	2.27	0.16	7.8E+07	2.6E+15