Crystal violet-modified Fe$_3$O$_4$@Au SERS probes: A novel highly sensitive method for H$_2$ detection

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Calculating the molecular density of CV-modified FA substrate surface：

(a) CV molecule on each FA microsphere

According to UV-vis experiment (Figure 2-e), the amount of CV molecular functionalized on 1 mL FA substrate was

$$N_{AM} = C_{CV} \times V_{CV} \approx (100.0 - 2.7) \times 10^{-6} \times 1 \times 10^{-3} \times 6.02 \times 10^{23} \approx 5.9 \times 10^{16}$$

There are 30mg $Fe_3O_4@SiO_2$（FS） in 1 mL FA substrate, the amount of FS was

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

$$\approx 4.0 \times 10^{11}$$

At the time of detection, the amount of 4μL FA particles on the silicon wafer is:

$$N_{FA} = 4.0 \times 10^{11} \times \frac{4 \times 10^{-3}}{3} \approx 5.3 \times 10^{8}$$

The amount of CV molecule functionalized on each FA sphere was

$$N_{CV} = \frac{N_{AM}}{N_{FA}} = \frac{5.9 \times 10^{16}}{5.3 \times 10^{8}} \approx 1.1 \times 10^{8}$$

(b) Surface area of each FA microsphere

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

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

Where Φ represents the deflection angle, Gap is distance between Au NPs, R is the radii of the FS NP, r is the radii of the Au NP (Figure 1-b). Here, Gap, R and r are experimentally determined as Gap=7 nm, R=155 nm and r =10 nm. Based on these parameters, we obtained that the amount of Au NPs bound to an FS sphere is about 587. Then surface area of each FA microsphere is abou1.08×10^6.

(c) CV density on FA surface

$$D_{AM} = \frac{N_{CV}}{S_{FA}} \approx \frac{1.1 \times 10^8}{1.08 \times 10^6} \approx 102 \; per \; nm^2$$

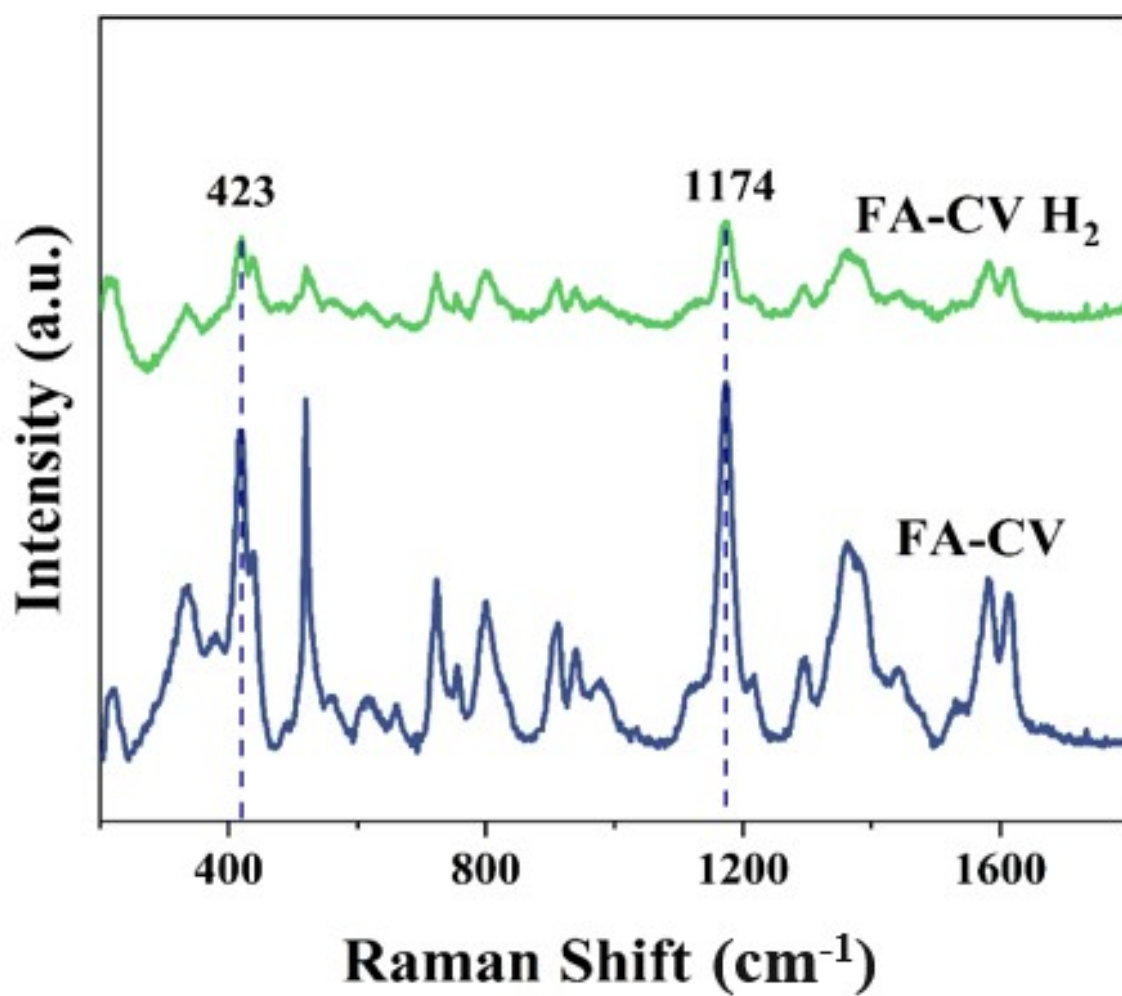The CV molecule density functionalized on each FA sphere can be estimated to be about 102 per nm^2.

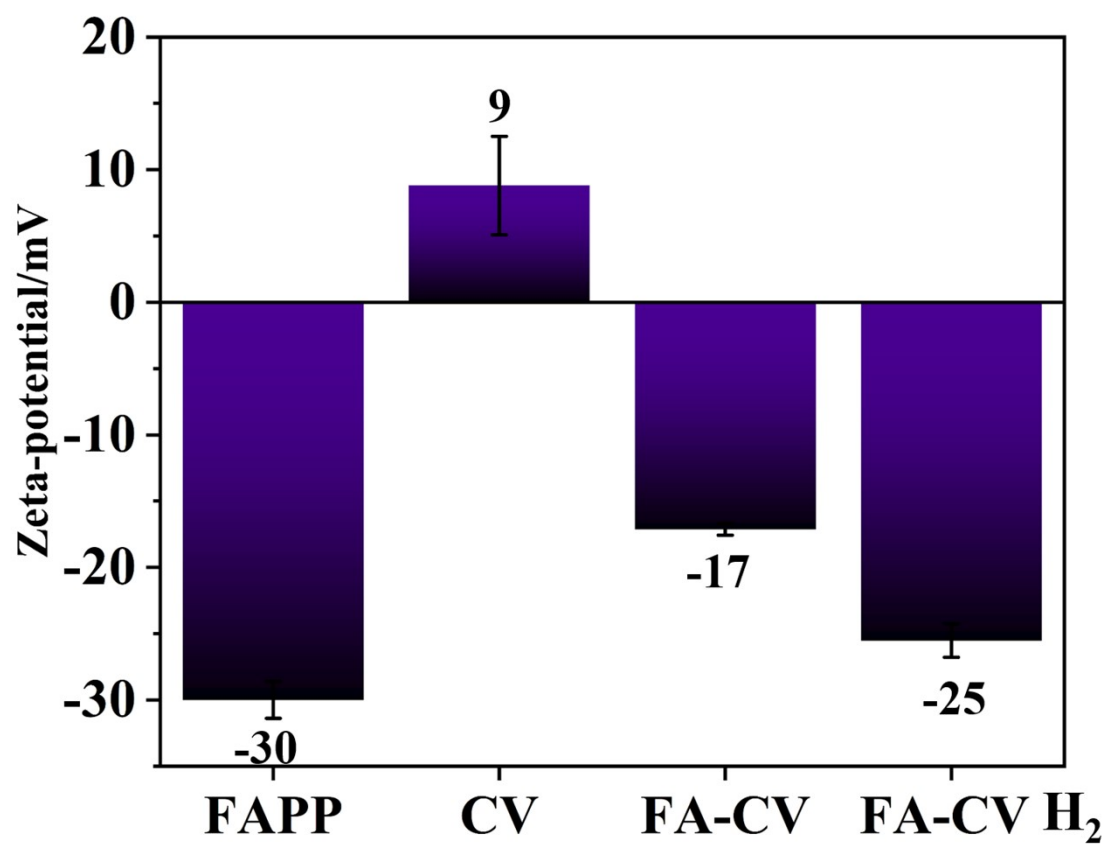Figure S1 SERS spectra of FA-CV and FA-CV after exposure to H_2.

Figure S2.Zeta potential measurements for FAPP, CV, FA-CV and FA-CV passes H_2.
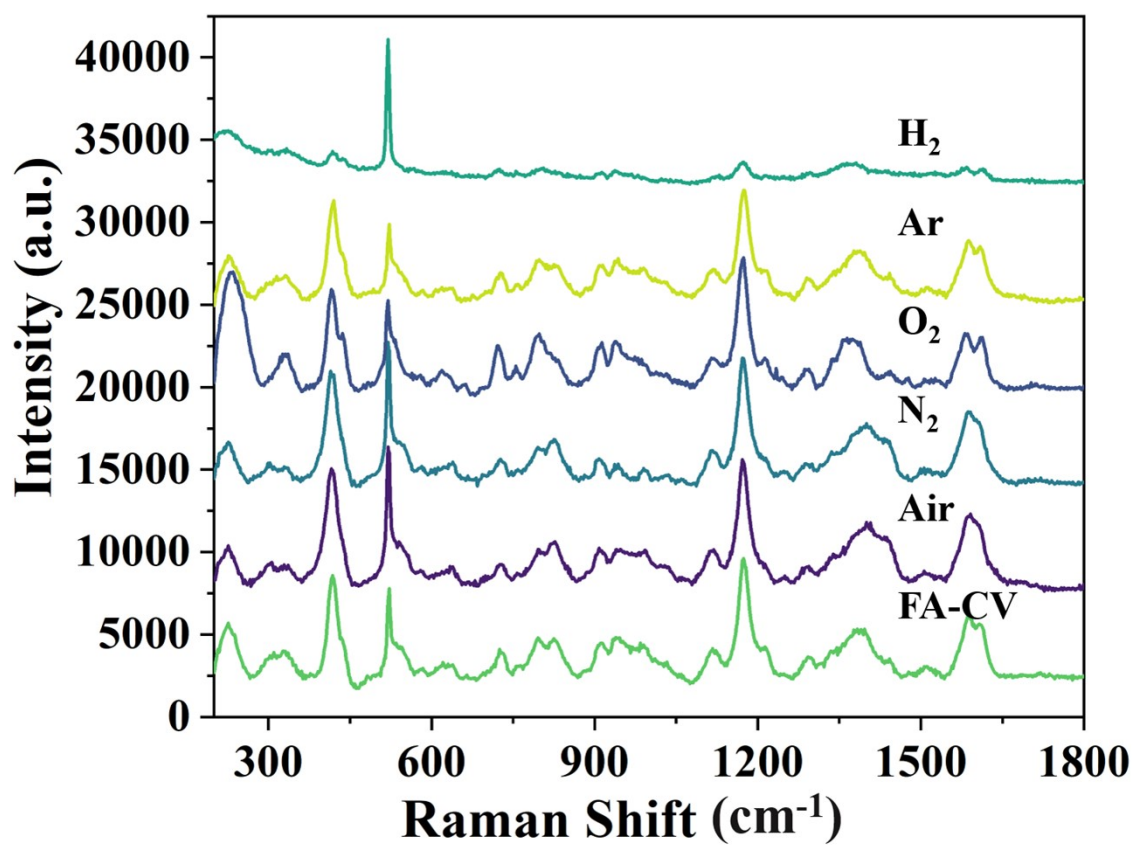
Figure S3 Raman spectra of FA-CV substrate under N_2, Ar, air, O_2 and H_2 ambient conditions.