A Synergistic Combination of Diatomaceous Earth with Au Nanoparticles as a Periodically Ordered, Button-like Substrate for SERS Analysis of the Chemical Composition of Eccrine Sweat in Latent Fingerprints

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## 1. Exploration of the appropriate amount of amino-functionalized diatomaceous earth templates used for the assembly of Au nanoparticles.

32±5.4 nm Au nanoparticles were used to explore the appropriate assembly parameter. 1 g, 0.1 g, 0.05 g, and 0.025 g of amino-functionalized diatomaceous earth were added into 100 mL of 32±5.4 nm Au nanoparticles solution with a mixture of 80% water and 20% ethanol, respectively. Figure S1a, S1b, S1c, and Figure 3b are their corresponding TEM images, showing that the loading of Au nanoparticles increases along with the decrease in the amount of the added amino-functionalized diatomaceous earth. When it came to the addition of 0.025 g of amino-functionalized diatomaceous earth, the formed diatomaceous earth-templated Au nanoparticle arrays exhibited heavy coverage of Au nanoparticles (Figure 3b), which was capable for surface-enhanced Raman spectroscopy (SERS) detection, so the amount of 0.025 g of amino-functionalized diatomaceous earth was chosen.



Figure S1 TEM images of (a) 1 g, (b) 0.1 g, and (c) 0.05 g of amino-functionalized diatomaceous earth was added into 100 mL of 32±5.4 nm Au nanoparticles solution with a mixture of 80% water and 20% ethanol, respectively.

## 2. Enhancement factors (EFs) calculation

Here, rhodamine 6G (R6G) was employed as the probe molecule.  $10^{-2}$  M of R6G solution was used for normal Raman detection, and 10 µL of  $10^{-4}$  M R6G solution was dropped onto the portable SERS tablets composed of diatomaceous earth-templated  $18\pm2.4$  and  $32\pm5.4$  nm Au nanoparticle arrays, respectively, for SERS detection.

The most widely used definition for EF is<sup>[1]</sup>

$$EF = \frac{I_{surf}}{I_{bulk}} \times \frac{N_{bulk}}{N_{surf}}$$

where  $I_{surf}$  and  $I_{bulk}$  are the integrated intensities of R6G molecules adsorbed on the portable SERS substrate and from 10<sup>-2</sup> M of R6G bulk solution, respectively.  $N_{surf}$  and  $N_{bulk}$  are the corresponding numbers of R6G molecules adsorbed on the portable SERS substrate and in the bulk solution effectively illuminated by the laser beam, respectively.

where *A* is the area of the laser focal spot, *h* is the confocal depth of the laser, and *h* is  $13 \Box \mu m$  according to our previous work,<sup>[2]</sup>  $c_{bulk}$  is the concentration of R6G bulk solution, here  $c_{bulk}=10^{-2}$  M,  $N_A$  is the Avogadro constant.

Provided that R6G molecules were in monolayer adsorption on the diatomaceous earth-templated Au nanoparticle arrays:

$$N_{surf} = \frac{c_{surf} v N_A A}{\pi r^2}$$

where  $c_{surf}$  is the concentration of R6G solution for SERS,  $c_{surf}=10^{-4}$  M, v is the volume of R6G solution used for SERS detection, v=10 µL, r is the radius of 10 µL of R6G solution formed on the SERS substrate, r=3.5 mm.

Figure S2a, S2b are the normal Raman spectrum of  $10^{-2}$  M of R6G solution and SERS spectrum of  $10^{-4}$  M of R6G solution acquired from the portable SERS tablet composed of diatomaceous earth-templated  $18\pm2.4$  nm Au nanoparticle arrays, respectively. The integrated intensities of the bands for  $I_{bulk}$  (1508 cm<sup>-1</sup>) and  $I_{surf}$  (1506 cm<sup>-1</sup>) are 1051 and 418424 cps, respectively. Considering the different incident laser

power for normal Raman spectrum and SERS spectrum acquisition, and the different number of molecules in each unit volume,<sup>[2]</sup>  $I_{surf}/I_{bulk}$ =418424×10<sup>4</sup>/1051.

Finally, the EF of the portable SERS tablet composed of diatomaceous earthtemplated  $18\pm2.4$  nm Au nanoparticle arrays was calculated as  $1.99\times10^7$ .

The integrated intensity of the band for  $I_{surf}$  (1506 cm<sup>-1</sup>) in Figure S2c is 583477 cps. Similarly, the EF of the portable SERS tablet composed of diatomaceous earth-templated 32±5.4 nm Au nanoparticle arrays was calculated as 2.78×10<sup>7</sup>. Each SERS spectrum in Figure S2b, S2c is an average result of the ten detections in Figure 4a, 4b, respectively.



Figure S2 (a) Normal Raman spectrum of  $10^{-2}$  M R6G solution. Laser power: 10 mW. SERS spectrum of  $10^{-4}$  M R6G solution acquired from the portable SERS tablets composed of diatomaceous earth-templated (b) 18±2.4 nm and (c) 32±5.4 nm Au nanoparticle arrays. Laser power: 0.1 mW.



Figure S3 FE-SEM images of the mass-equivalent amount of (a)  $18\pm2.4$  and (b)  $32\pm5.4$  nm Au nanoparticle covered glass substrates. SERS spectra of  $10^{-4}$  M R6G solution acquired from 10 random spots on the mass-equivalent amount of (c)  $18\pm2.4$  and (d)  $32\pm5.4$  nm Au nanoparticle covered glass substrates. Excitation wavelength: 638 nm; laser power: 0.1 mW. (e) Plots of the peak intensities of R6G at 773 cm<sup>-1</sup> obtained from 10 random spots on the abovementioned  $18\pm2.4$  and  $32\pm5.4$  nm Au nanoparticle covered glass substrates.





Figure S4 TEM images of the diatomaceous earth-templated (a)  $18\pm2.4$  and (b)  $32\pm5.4$  nm Au nanoparticle arrays, showing that the Au nanoparticles not only adsorb on the surface but also around the pores of the diatomaceous earth.

## References

[1] Le Ru, E. C.; Blackie, E.; Meyer, M.; Etchegoin, P. G. J. Phys. Chem. C 2007,

111, 13794-13803.

[2] Chen, J.; Shen, B.; Qin, G. W.; Hu, X. W.; Qian, L. H.; Wang, Z. W.; Li, S.; Ren,

Y. P.; Zuo, L. J. Phys. Chem. C 2012, 116, 3320-3328.