Supporting Information

Chemical visualization of sweat pores in fingerprints using GO-enhanced TOF-SIMS

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Preparation of GO layer

A Si wafer (14 mm × 10 mm) was washed by water, dichloromethane, acetone and methanol. For the preparation of GO layer on Si wafer, a Si wafer was immersed in GO solution and then dried on oven at 60 ℃ for 6 hours. The concentration of GO solution has significant influence on the final morphology of GO layer. Both low (< 1 mg/mL) and high (> 3 mg/mL) concentration of GO solution would result in the non-uniform thickness of GO layer. A smooth and even GO layer could be obtained by using a GO solution as appropriate concentration (2 mg/mL in this work). The thickness of GO layer was about 2 μm, measured by a commercial step profiler (see Figure S1).

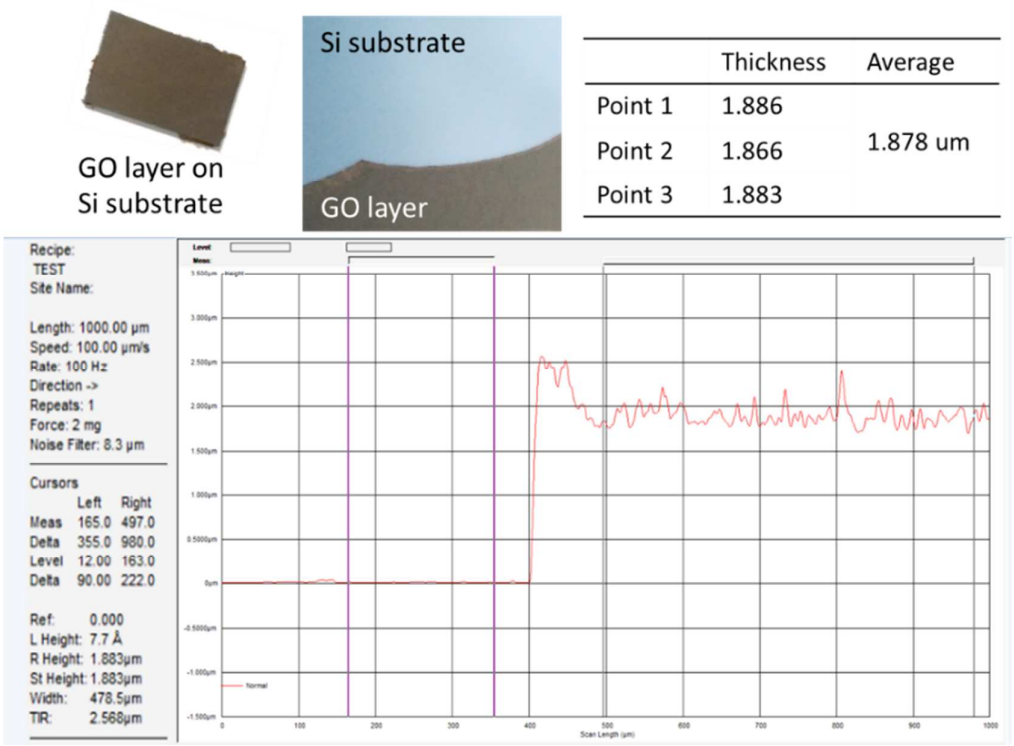

Figure S1. A measurement of GO layer thickness was carried out using AMBIOSXP-1 step profiler (AMBIOS, USA). The thickness of GO layer on Si substrate was about 2 μm as an average of 3 test points. A data graph of point 3 was showed.

Increased molecular ion signals of other high-mass molecules

To evaluate the enhancement effect of GO matrix to different kinds of chemicals, lipids and peptides solutions were also analysed. The results showed that molecular ion signals of such molecules (~700-1000 Da) increased largely with the use of GO. These three lipids have very similar SIMS spectra at low mass range, because they possess the same head group, thus forming same fragmental ions under primary ion beam bombardment. They could be distinguished and identified according to their molecular ions, which also implies the importance of the usage of GO matrix. It demonstrated that GO increased the secondary ion yields of high-mass molecular ions from different kinds of chemicals, thus holed the potentials in identification of a wider variety of chemicals in fingerprints.

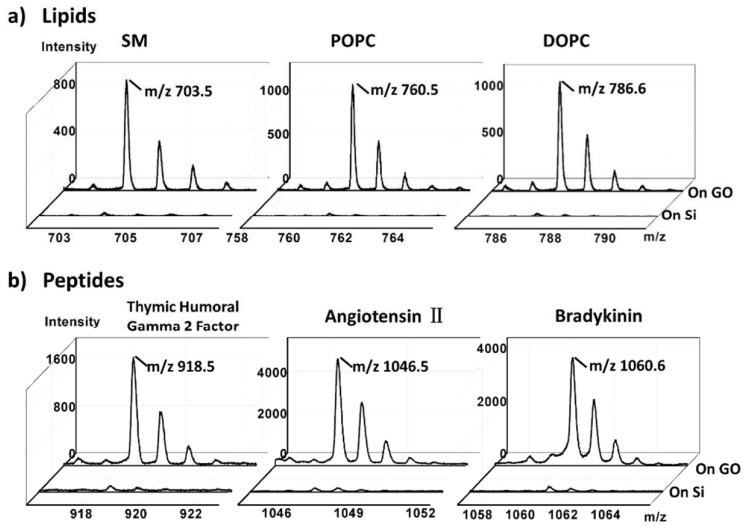

Figure S2. Molecular ion peaks in positive ion mode from a) lipids mixture solution and b) peptides mixture solution on a GO layer (top line) or Si substrate (bottom line). Lipids, 1-palmitoyl-2-oleoyl-snglycero-3-phosphocholine (POPC), 1,2-dioleoyl-snglycero-3-phosphocholine (DOPC) and sphingomyelin d18:0/16:1 (SM) at m/z 703.5 were purchased from Sigma Aldrich (St. Louis, MO, USA) and peptides were purchased from China Peptides (Shanghai, China).

Imaging metal ions in fingerprints on Si substrate

Without the usage of GO matrix, molecular ion signals in high-mass range were so weak in SIMS spectra. Only the metal ions such as K^+ and Na^+ and some fragmental ions from organic such as CH_3^+, $C_2H_3^+$ and $C_2H_5^+$ could be used to image the fingerprints. We imaged K^+ and Na^+ in two fingerprints after contact with different drugs. Mapping K^+ and Na^+ could show clear pattern in both fingerprints. The sweat pores in a ridge could also be clearly observed by mapping K^+ and Na^+. However, such metal ions are widespread in fingerprints and thus mapping such metal ions could only be used in pattern recognition. The molecular ions of drugs were insufficient to image the fingerprints and thus weakened the superiority of TOF-SIMS as a chemical imaging tool in fingerprint analysis.

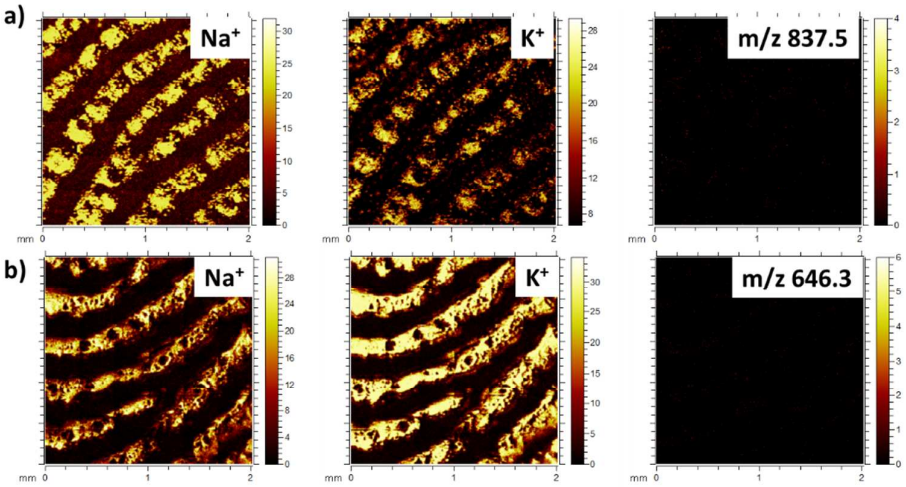

Figure S3. a) Mapping Na^+, K^+ and molecular ions of azithromycin in fingerprints contaminated by azithromycin solution and left on Si substrate. b) Mapping Na^+, K^+ and molecular ions of aconitine in fingerprints contaminated by aconitine solution and left on Si substrate. Scan area: 2.0×2.0 mm^2.

Multi-components identification and overlapping fingerprints analysis

Using TOF-SIMS, multi-components in fingerprint could be detected at the same time. For example, when a fingerprint was left on GO layer after contact with a mixture containing three compositions, we could observe three intense peaks in high-mass range in one

TOF-SIMS spectrum (not shown), which were identified as the molecular ions of three drugs, erythromycin, azithromycin and roxithromycin respectively. These molecular ions could be imaged at the same time (Figure S4). This protocol showed potentials in such applications as simultaneous multi-components analysis in fingerprints. Moreover, GO-enhanced TOF-SIMS could be used to distinguish the overlapping fingerprints with high spatial resolution images. The chemical information could be extracted from each fingerprint, which may help to link the suspects to their identity and criminal activities.

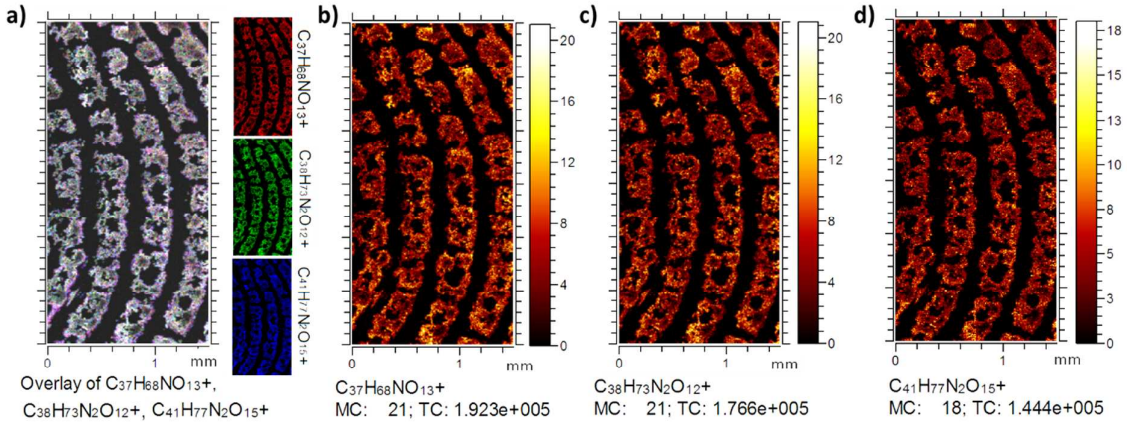

Figure S4. Mapping molecular ions of three antibiotics in a fingerprint. a) RGB overlay of m/z 734.5 (red, assigned to $C_{37}H_{68}NO_{13}^{+}$), 749.5 (green, $C_{38}H_{73}N_2O_{12}^{+}$) and 837.5 (blue, $C_{41}H_{77}N_2O_{15}^{+}$), b) SIMS 2D image of molecular ions of erythromycin at m/z 734.5, (c) azithromycin at m/z 749.5 and (d) roxithromycin at m/z 837.5. Scan area: 1.5 × 3.0 mm^2.

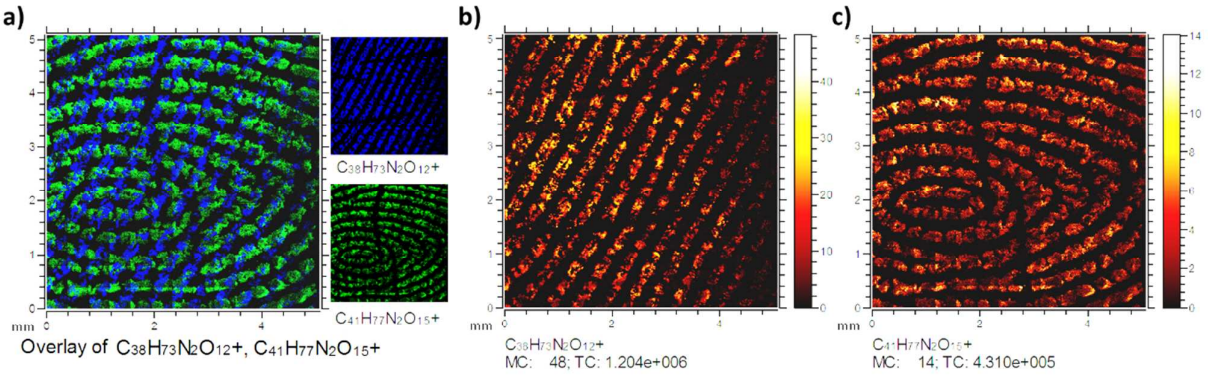

Figure S5. Mapping molecular ions of two antibiotics in overlapping fingerprints. a) RGB overlay of m/z 749.5 (green, assigned to $C_{38}H_{73}N_2O_{12}^{+}$) and 837.5 (blue, $C_{41}H_{77}N_2O_{15}^{+}$), b) SIMS 2D image of molecular ions of azithromycin at m/z 749.5 and (c) roxithromycin at m/z 837.5.

Simple transfer of fingerprints from crime scene to a GO layer

To develop the actual application of GO-enhanced TOF-SIMS in criminal investigation, high-mass molecules in fingerprints in an assumed crime scene could be detected by TOF-SIMS, via a simple transfer from scene to a GO layer. Firstly, a fingerprint was left on a glass surface and then a GO layer was impressed on the fingerprint under a pressure for a few seconds. When the GO layer was send to analyzed by TOF-SIMS, we could obtain the pattern and chemical information of this fingerprint. This protocol solved a problem that the size of sample was limited because of the limited volume of SIMS vacuum chamber. The fingerprints left on assumed criminal scene, such as on a glass window or a stair railing could be transferred to GO layer surface. High-mass chemicals in fingerprints (azithromycin in this test) could thus be identified by their molecular ions. Mapping such molecular ions could also show the clear pattern of the fingerprint. The evaluation of transfer efficiency and optimization of experimental conditions are under study. However, this protocol holds potentials in such applications as fingerprint extraction and detection.

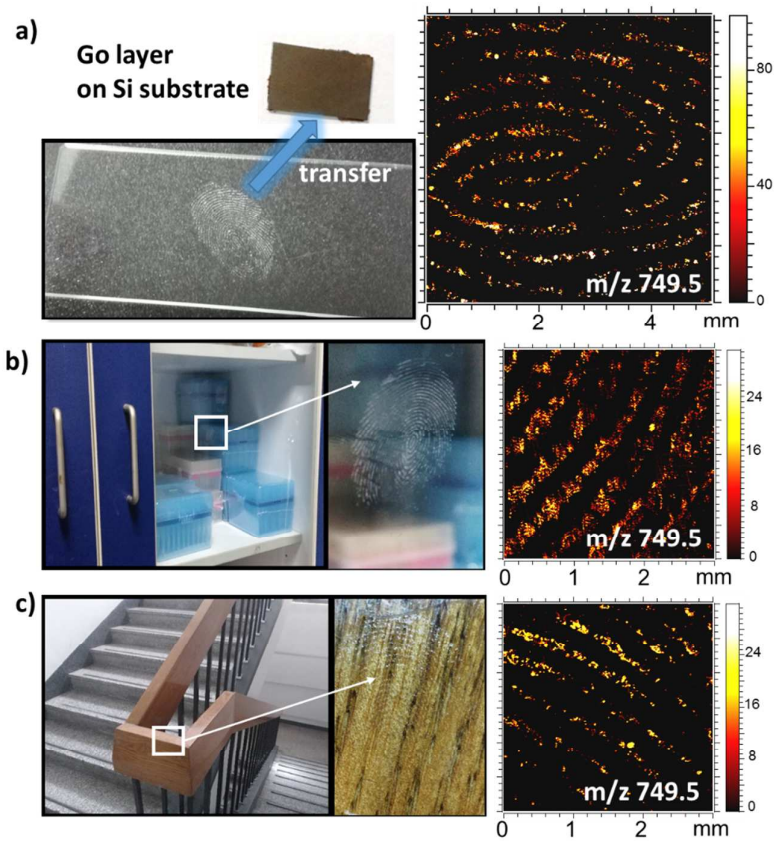

Figure S6. Some of contaminants in a fingerprint on other substrates could be transferred to GO layer by simple contact under a pressure. 2D TOF-SIMS images of molecular ions of azithromycin could be obtained on GO layer, which after contact with a fingerprint contaminated by azithromycin on a) a glass slide, b) a glass window and c) a stair railing.

Supplementary Tables

Table S1. Analysis of alkaloids and antibiotics standard samples on GO layer or Si substrate in TOF-SIMS.

Species	Substrate	$[M+H]^+$ Counts	Total Counts	$[M+H]^+$ /Total Counts	[M/T Ratio (on GO)] / [M/T Ratio (on Si)]
Hypaconitine	GO	143824	4.54E7	3.17E-03	11
	Si	8180	2.91E7	2.81E-04	
Mesaconitine	GO	380030	2.78E7	13.67E-3	28
	Si	7713	1.60E7	4.82E-4	
Aconitine	GO	254205	4.56E7	5.57E-3	12
	Si	4718	9.84E6	4.79E-4	
Erythromycin	GO	159489	6.91E7	2.31E-03	16
	Si	4531	3.10E7	1.46E-04	
Azithromycin	GO	191782	6.91E7	2.78E-3	23
	Si	3799	3.10E7	1.22E-4	
Roxithromycin	GO	158856	6.91E7	2.30E-3	37
	Si	1905	3.10E7	6.14E-5	

Table S2. Identifiable Peaks of alkaloids and antibiotics in Positive Ion Mode Spectra in TOF-SIMS.

Mass (m/z)	Composition	Deviation (ppm)	Species	Possible biomolecule
616.3202	$C_{33}H_{45}NO_{10}$	13.9	$[M+H]^+$	Hypaconitine
632.3097	$C_{33}H_{45}NO_{11}$	5.1	$[M+H]^+$	Mesaconitine
646.3218	$C_{34}H_{47}NO_{11}$	2.7	$[M+H]^+$	Aconitine
734.4649	$C_{37}H_{67}NO_{13}$	-4.9	$[M+H]^+$	Erythromycin
749.5058	$C_{38}H_{72}N_2O_{12}$	-13.4	$[M+H]^+$	Azithromycin
837.5239	$C_{41}H_{76}N_2O_{15}$	-9.5	$[M+H]^+$	Roxithromycin