Electronic Supplementary Material (ESI) for Chemical Science.

Supporting Information

Hybrid CuCoO-GO Enables Ultrasensitive Detection of Antibiotics with Enhanced Laser Desoprtion/Ionization at Nano-interfaces

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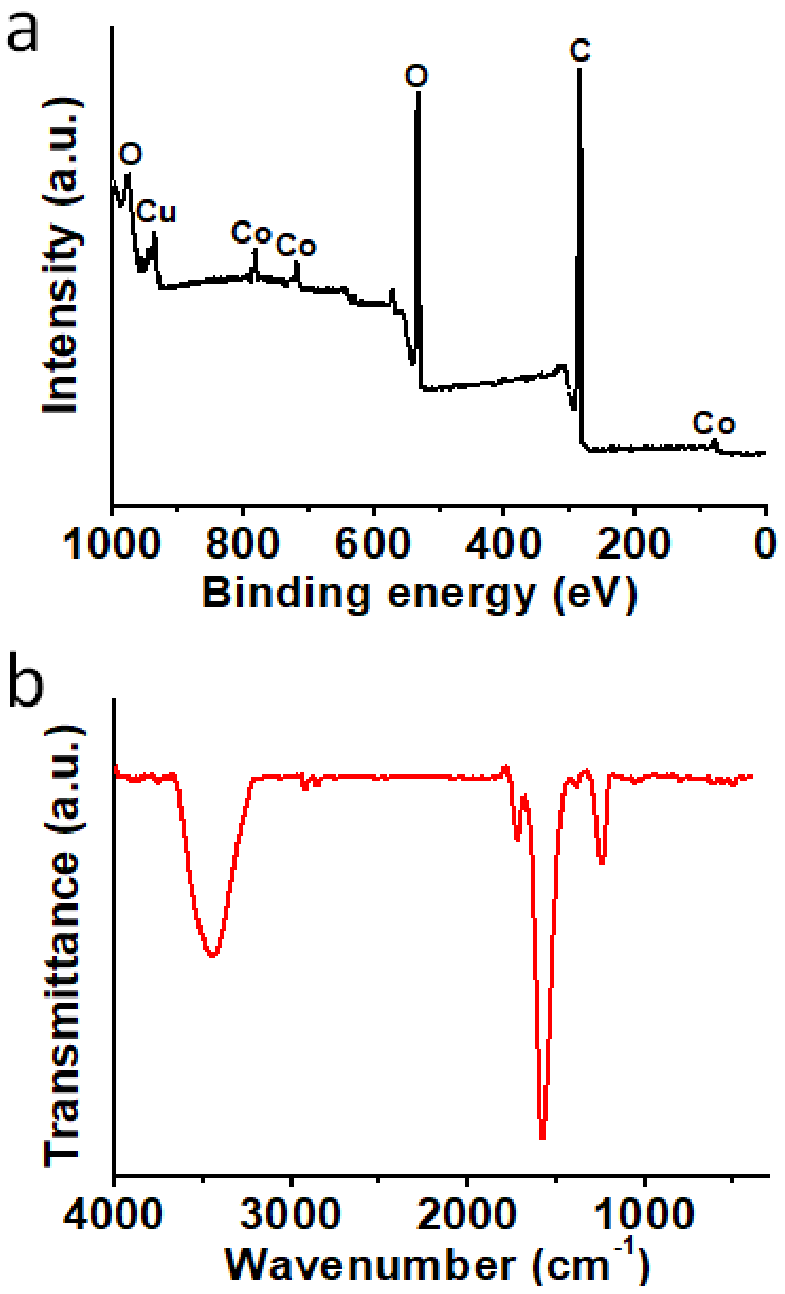


Fig. S1 (a) XPS spectrum of CuCoO-GO, with the peaks attributed to O, C, Cu and Co element as specified. (b) FTIR spectrum of CuCoO-GO. The peaks at 3400 cm^{-1} and 1570 cm^{-1} were contributed by the O–H and C=O stretching mode. The peak at 1250 cm^{-1} was attributed to the epoxy groups.

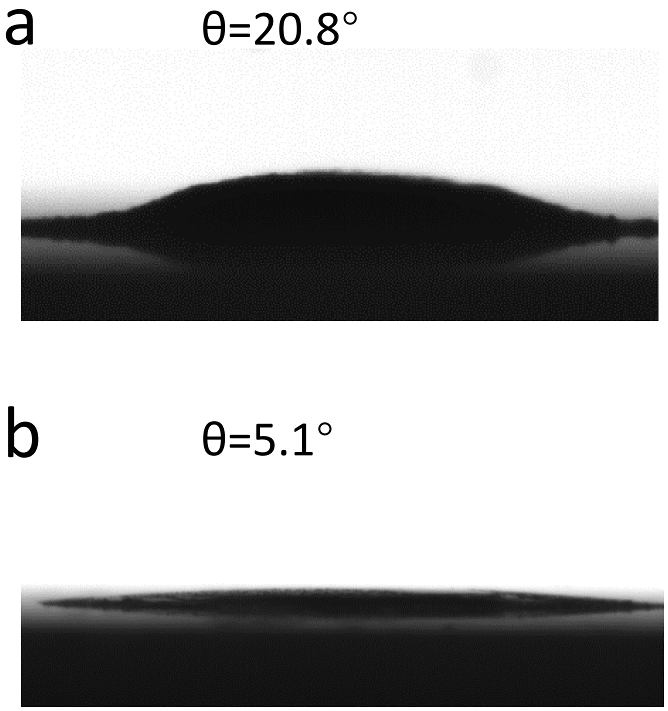


Fig. S2 The contact angle measurements of (a) GO, (b) CuCoO-GO. The images were recorded by contact angle measurement instrument (DataPhysics OCA).

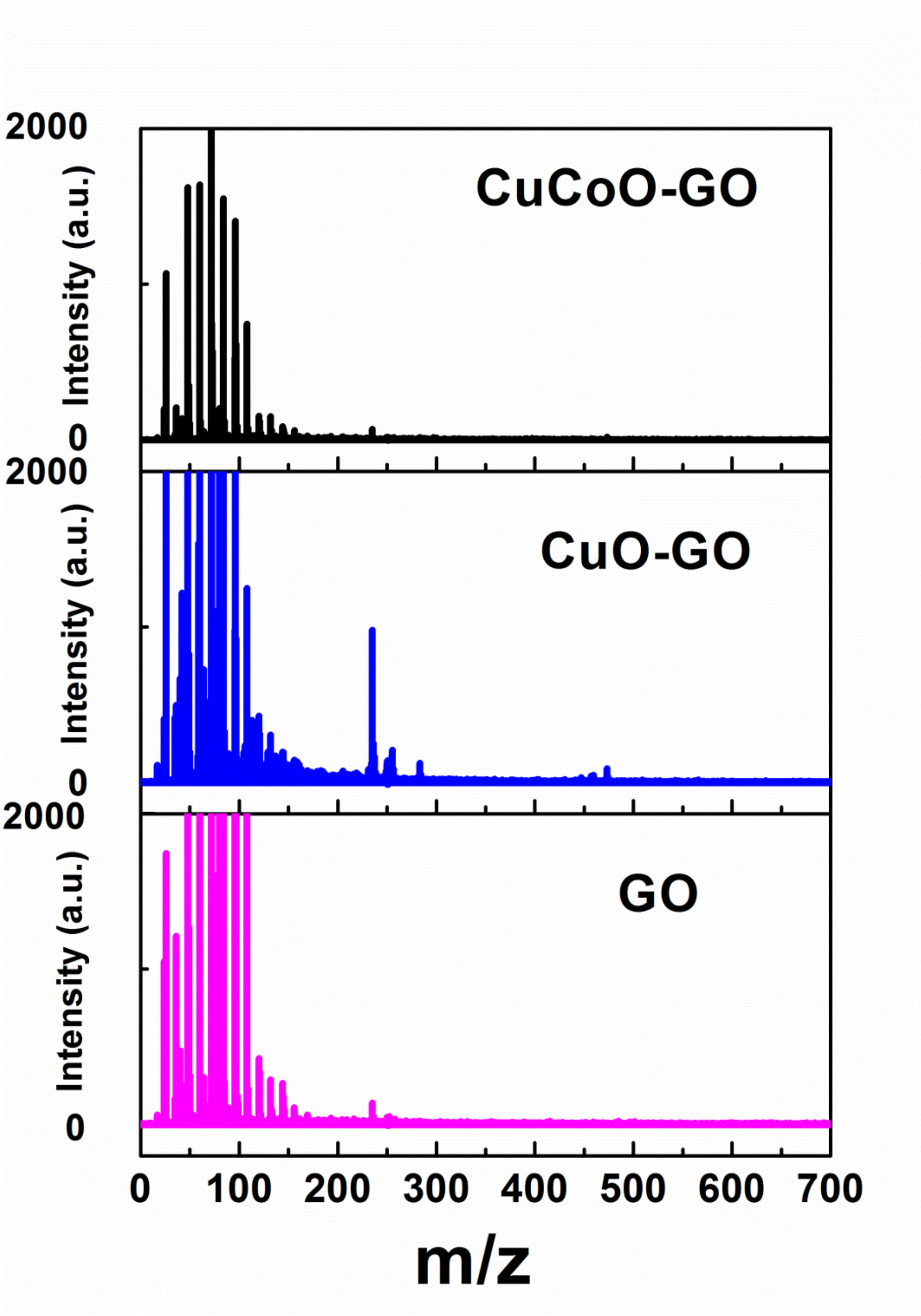


Fig. S3 The background noise of CuCoO-GO, CuO-GO, GO matrices in the negative-ion mode. There are some background noise in the range of m/z 0~150 for all of the three types of matrices. Noteworthy, the noise baseline of CuCoO-GO is lower than that of GO by several folds under the identical laser pulse energy level. The laser spot size was approximately 50~100 μm. The accumulation of 3000 laser shots was applied for each spectrum.

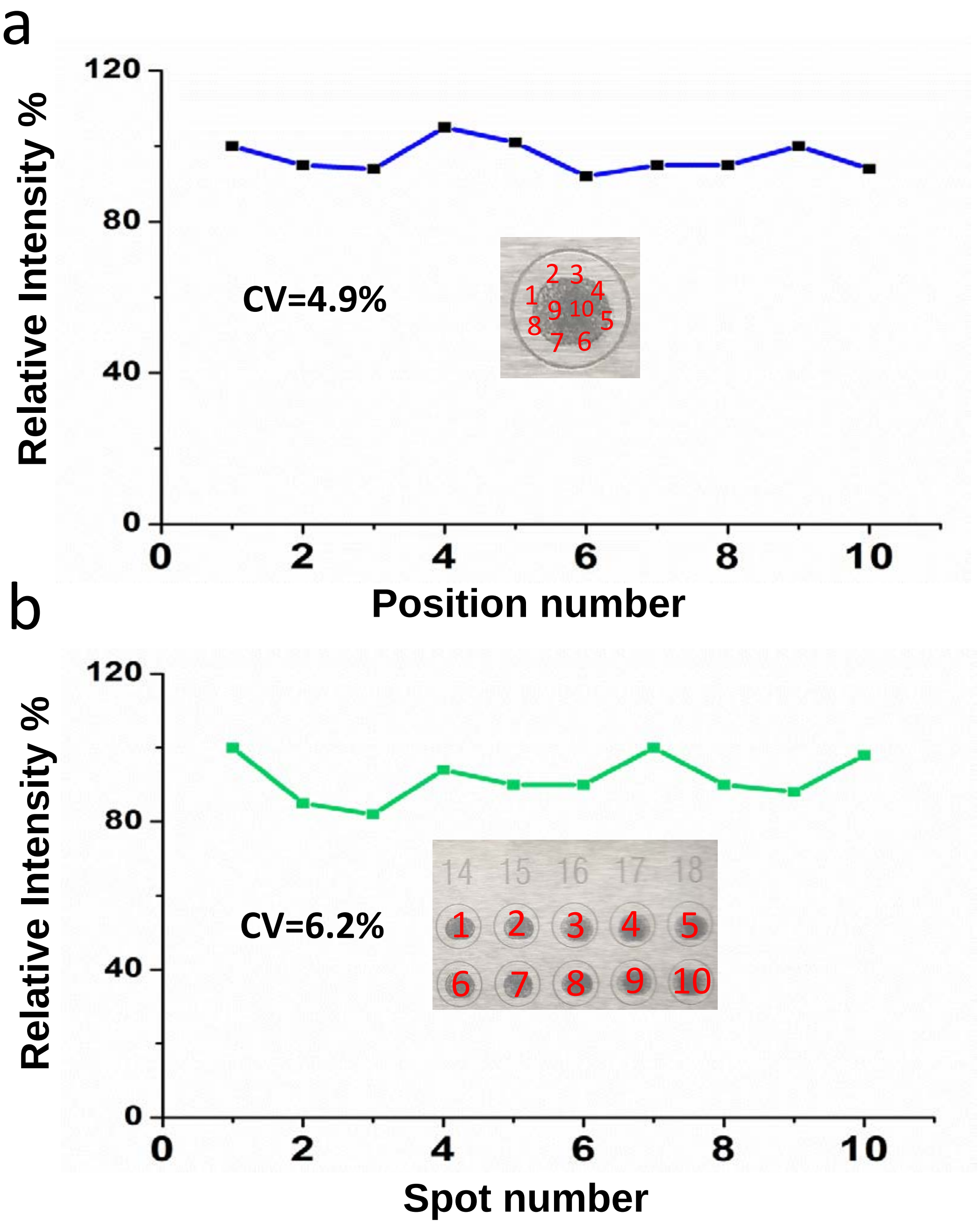


Fig. S4 Highly reproducible MS signals by using the CuCoO-GO matrix. Analyte: SDZ. (a) 10 different positions in a single spot. (B) 10 different spots in the 2×5 array. The coefficient of variation (CV) values: only 4.9% in the position-to-position tests (a) or 6.2% in the spot-to-spot tests (b).

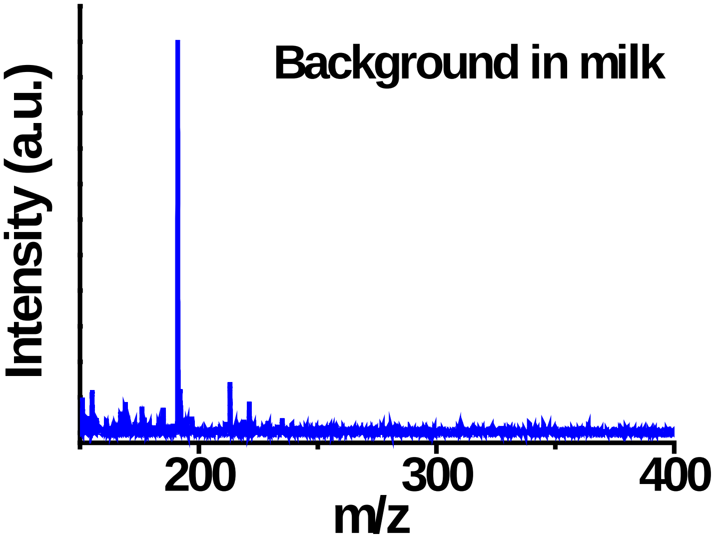
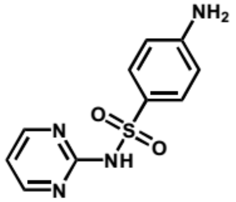
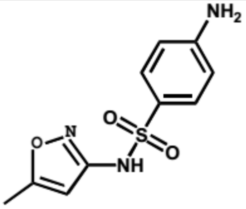
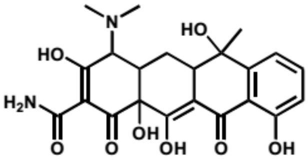
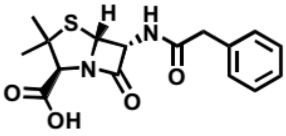
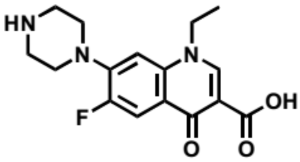
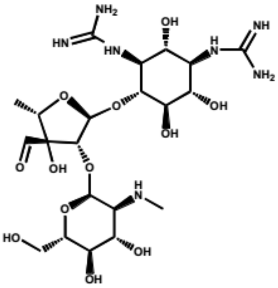
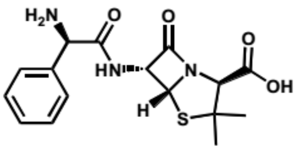
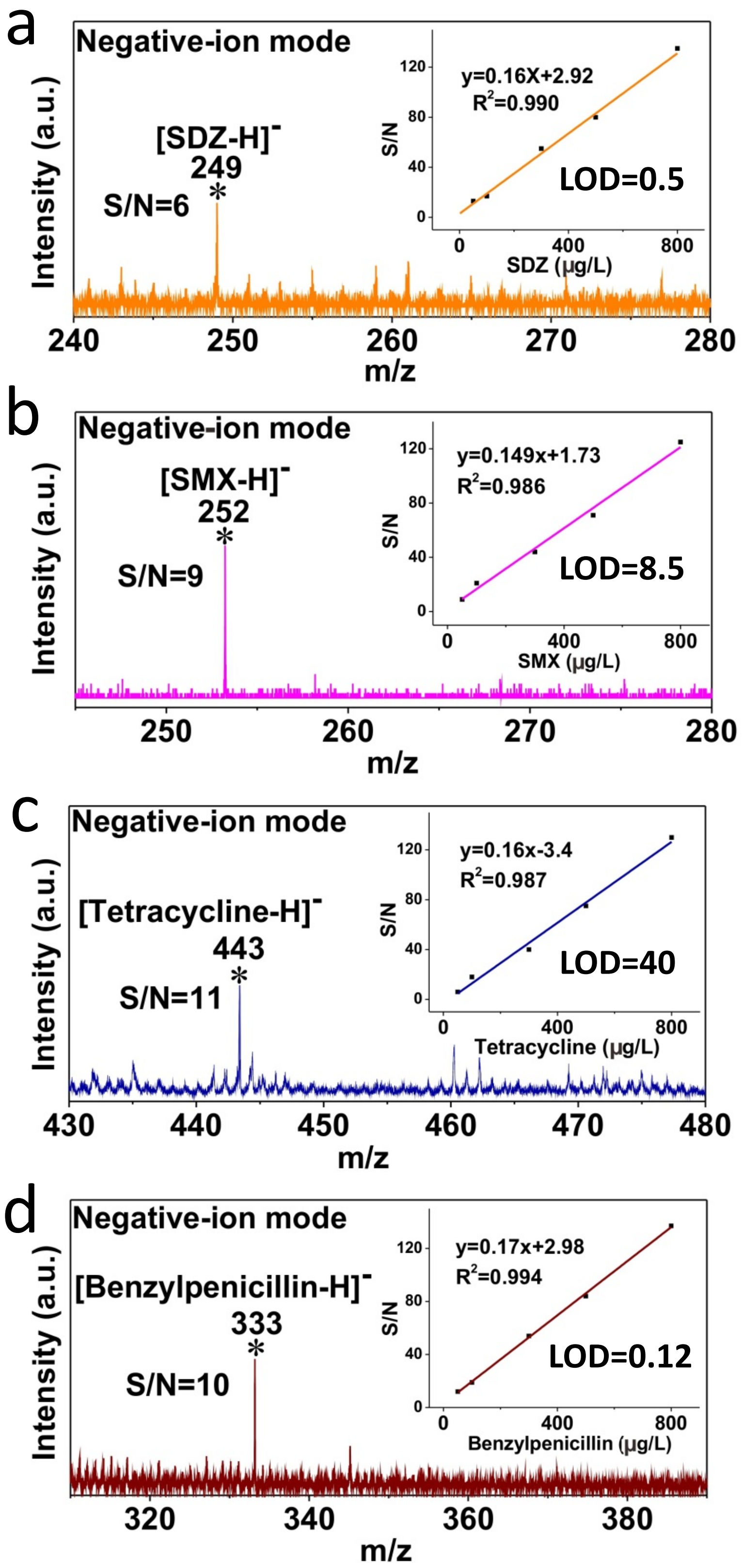


Fig. S5 MALDI-TOF-MS spectra of milk sample without analyte in the negative-ion mode with CuCoO-GO matrix.

Table S1. MRL and LOD values of the different antibiotics in reported literature and in our work by using CuCoO-GO as matrix.

Antibiotics	Structure	MRL (ug/L)	Others matrix LOD (ug/L)	Our Work LOD (ug/L)	Ref.
Sulfadiazine		100	250	0.5	15
Sulfamethoxazole		100	203	8.5	15
Tetracycline		100	79.9	40	38
Benzylpenicillin		4	0.4	0.12	39
Norfloxacin		100	11.1	5.8	40
Streptomycin		200	87	23	41
Ampicillin		4	1.4×10^3	2.7	42


a
Negative-ion mode
Intensity (a.u.)
[SDZ-H]⁻
249
S/N=6
m/z
240
250
260
270
280
y=0.16X+2.92
R²=0.990
LOD=0.5
S/N
SDZ (μg/L)
b
Negative-ion mode
[SMX-H]⁻
252
S/N=9
m/z
y=0.149x+1.73
R²=0.986
LOD=8.5
SMX (μg/L)
c
Negative-ion mode
[Tetracycline-H]⁻
443
S/N=11
m/z
430
440
450
460
470
480
y=0.16x-3.4
R²=0.987
LOD=40
Tetracycline (μg/L)
d
Negative-ion mode
[Benzylpenicillin-H]⁻
333
S/N=10
m/z
320
340
360
380
y=0.17x+2.98
R²=0.994
LOD=0.12
Benzylpenicillin (μg/L)

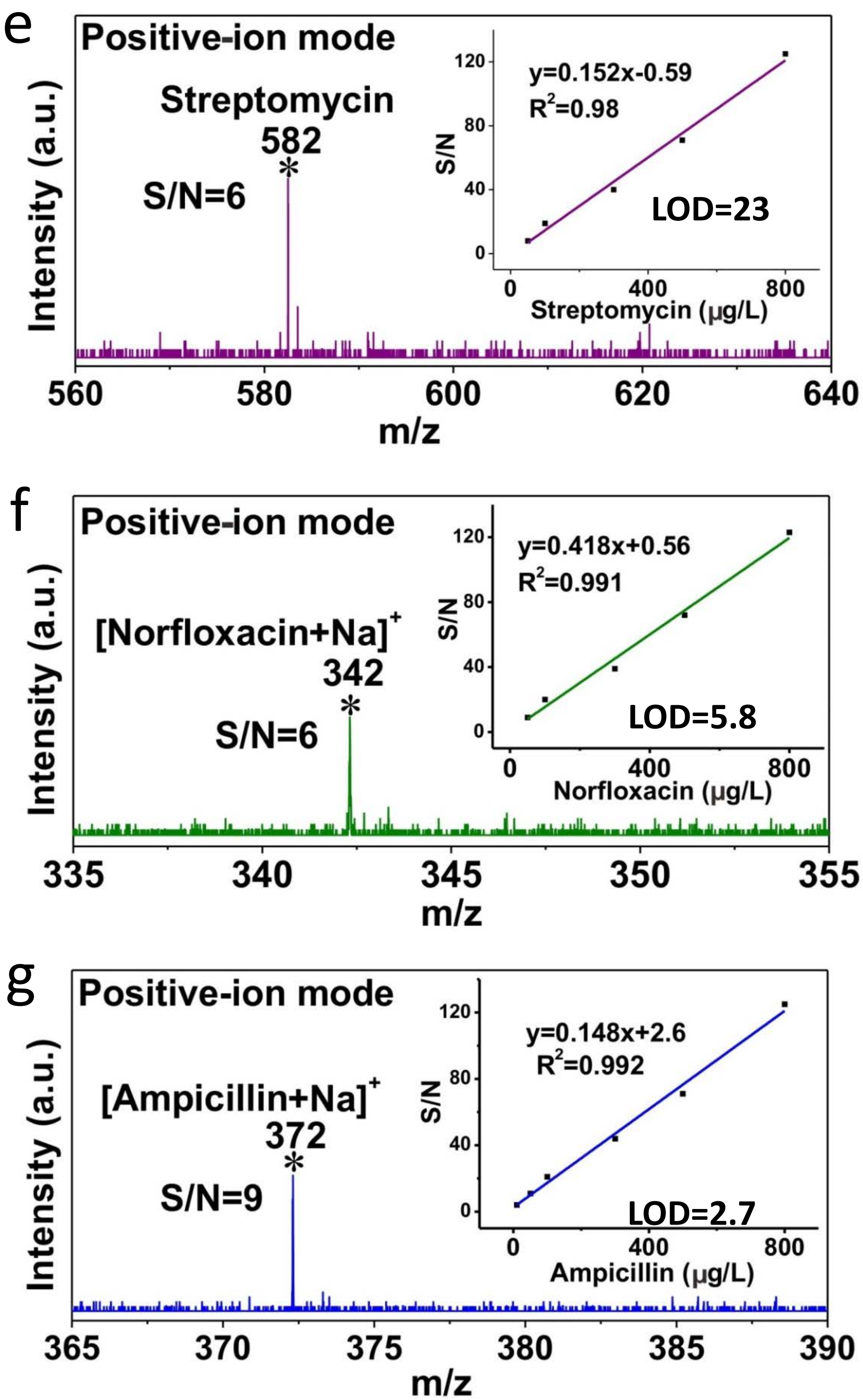


Fig. S6 MALDI-TOF mass spectra of seven antibiotics (a-g, as specified in the legend) using CuCoO-GO matrix. Inset: The linear fitting curves and corresponding LOD values (μg/L).

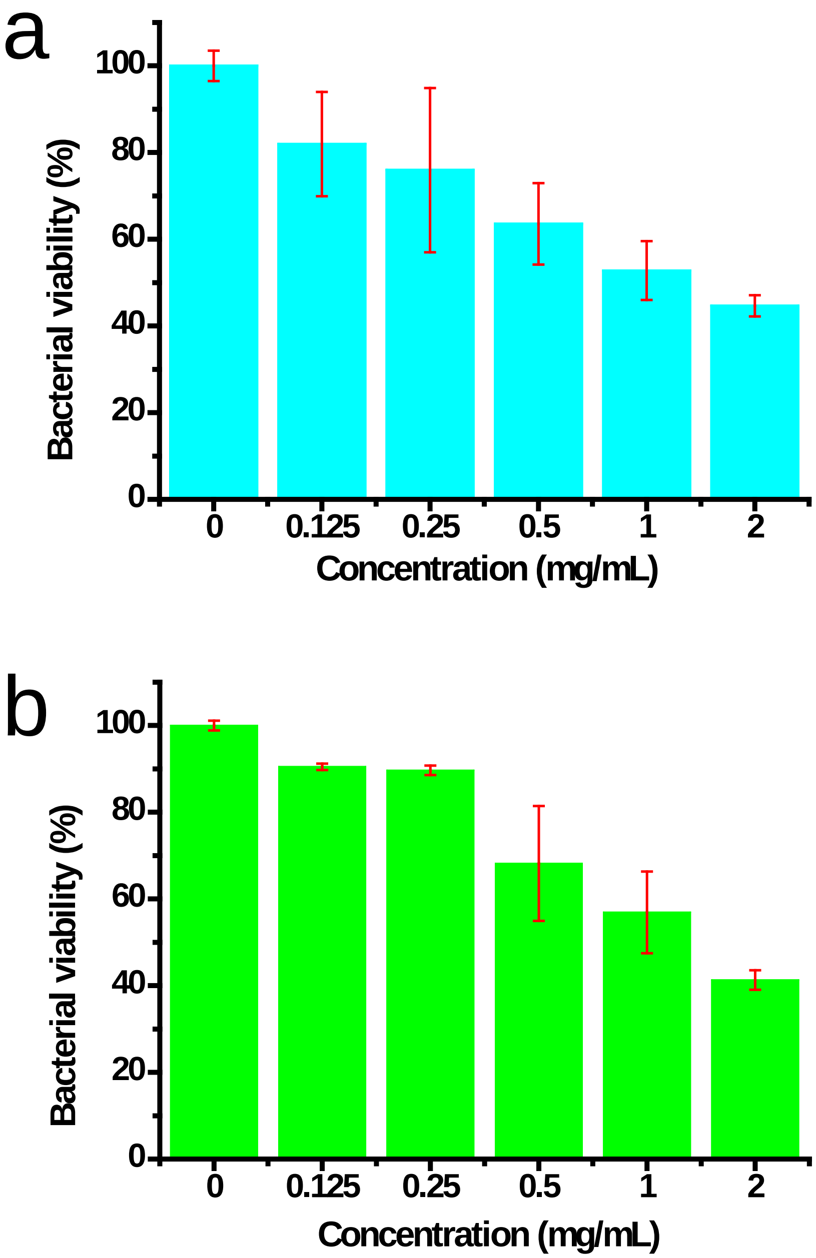


Fig. S7 Bacterial viabilities of (a) *E.coli* and (b) *S.aureus* incubated with SDS at the specified concentrations, according to the broth dilution test in standard AST epxeriments. OD600 values of the solutions were recorded by a Varioskan Flash (Thermo Scientific Company, USA). The bacterial samples incubated without SDS were used as the the blank control for normalization. The MIC_{50} values were determined to be nearly 1 mg/mL or 2 mg/mL for *E.coli* and *S.aureus* respectively. Each data points were collected from 2 separate batches. Each of the batches contained a repetition of 4 in parallel. Error bar: standard deviation.

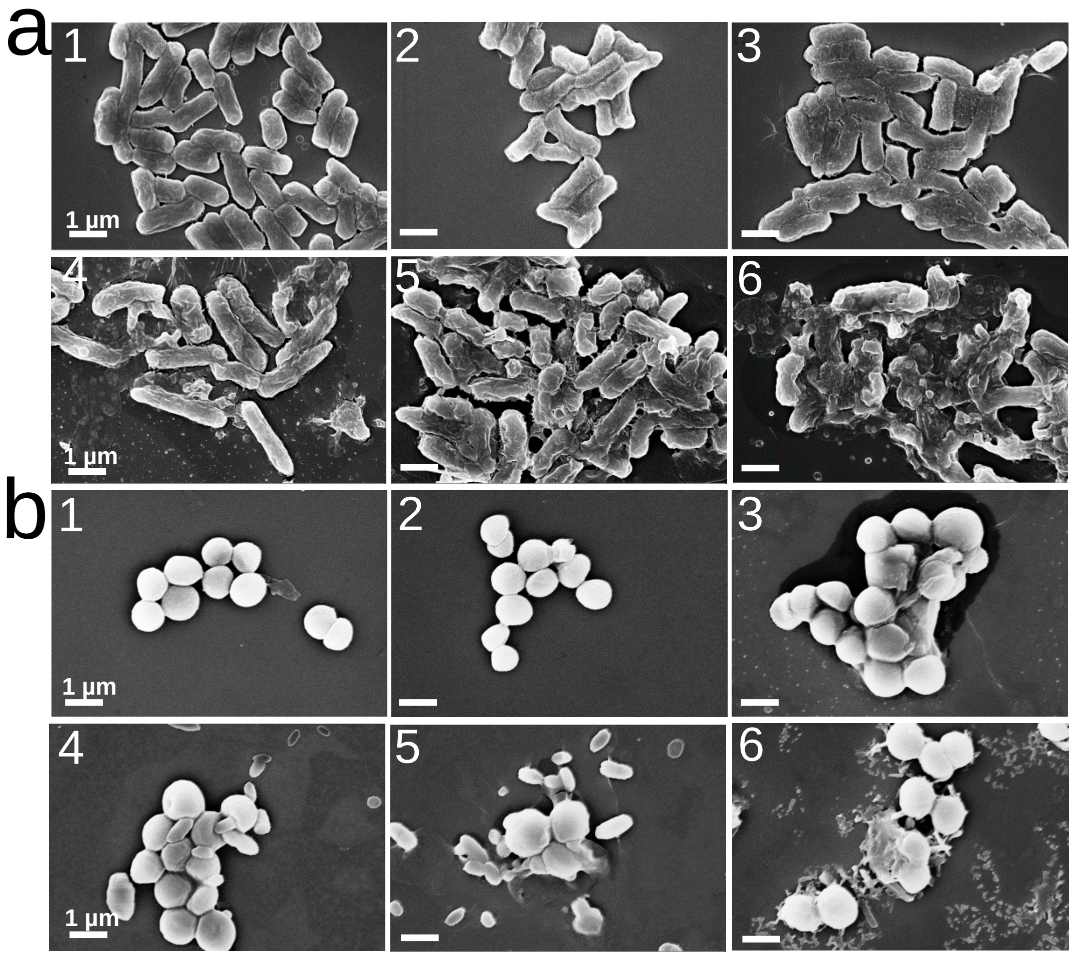


Fig. S8 Scanning electron microscope (SEM) images of (a) *E. coli* and (b) *S. aureus* after incubation with different concentrations of SDS. SDS concentrations in the images #1 ~ #6: 0, 0.125, 0.25, 0.5, 1, 2 mg / mL, respectively.

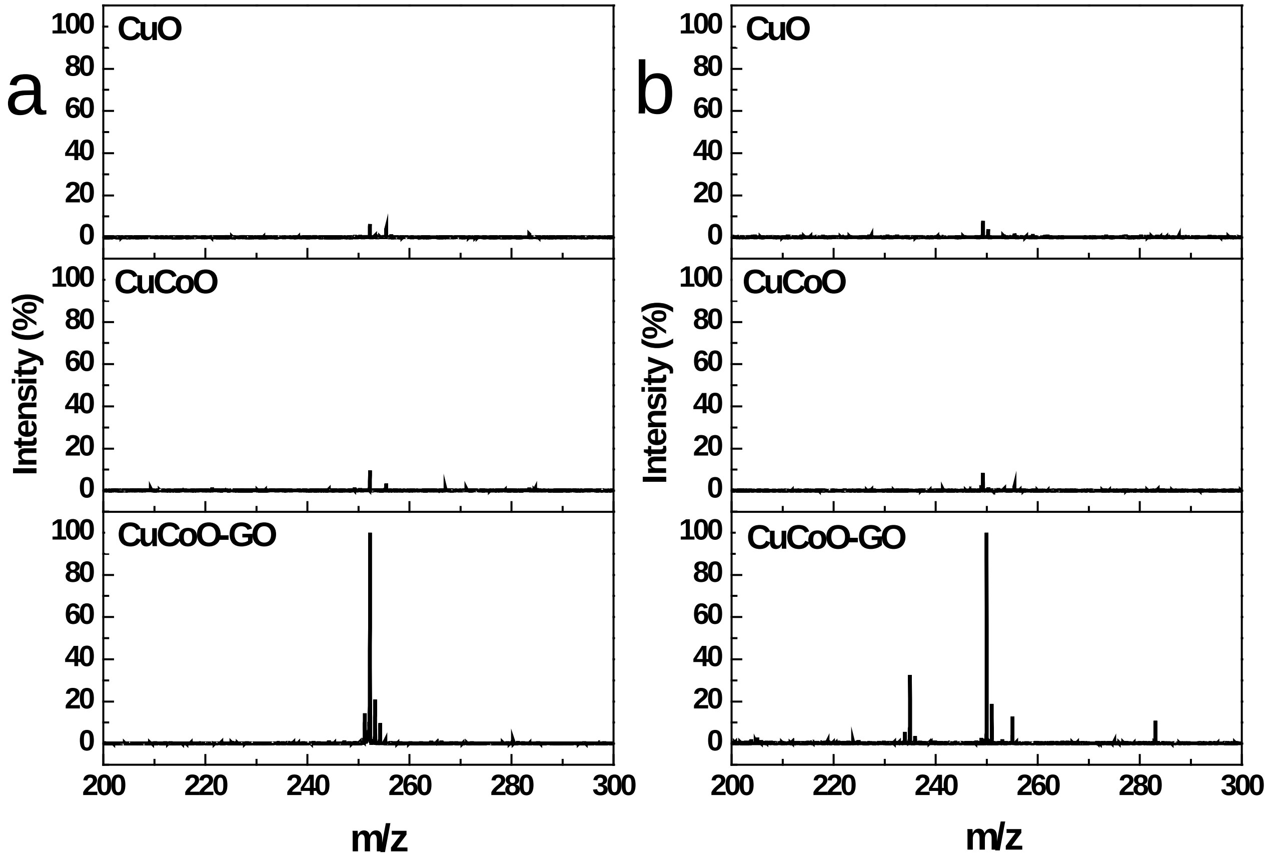


Fig. S9 Mass spectra of SMX (a) and SDZ (b) using CuO, CuCoO, and CuCoO-GO matrices. The MALDI MS detection was performed in the negative-ion mode. The laser spot size was approximately 50~100 µm. The accumulation of 3000 laser shots was applied for each spectrum.

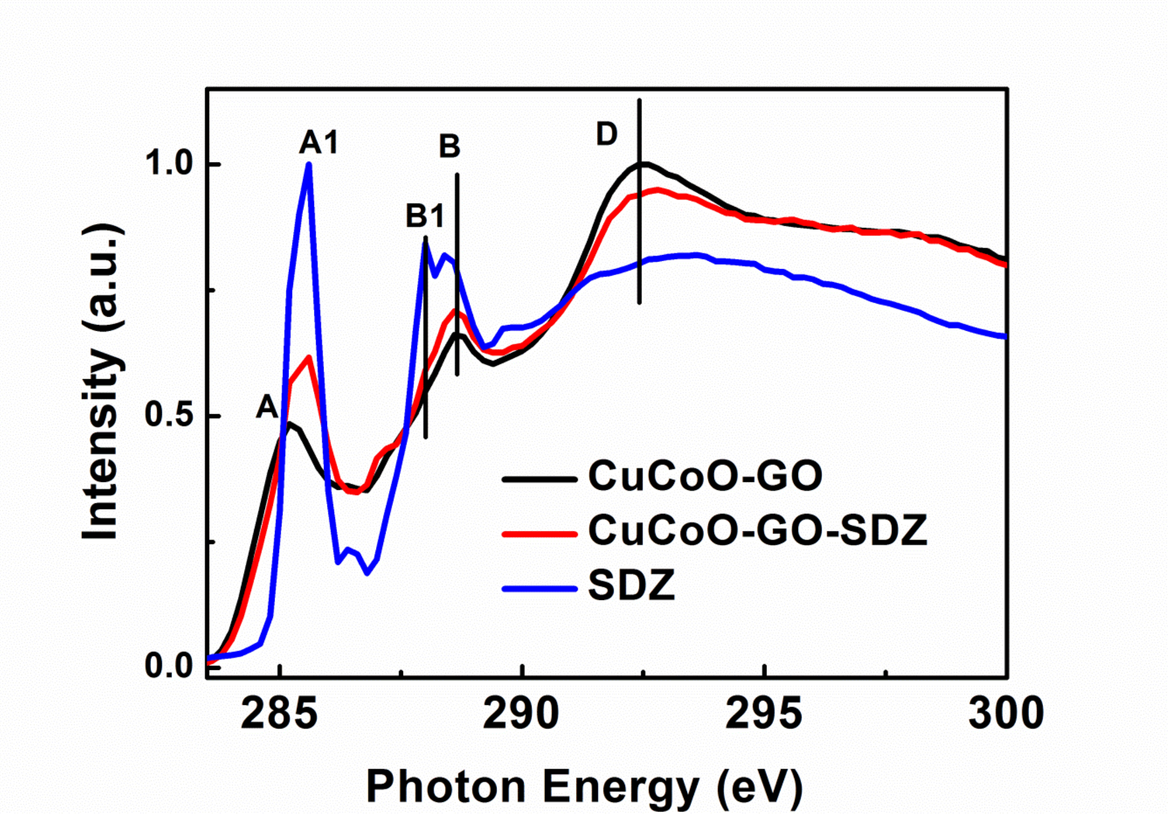


Fig. S10 XAS spectra of SDZ, CuCoO-GO and CuCoO-GO-SDZ at C K-edge.

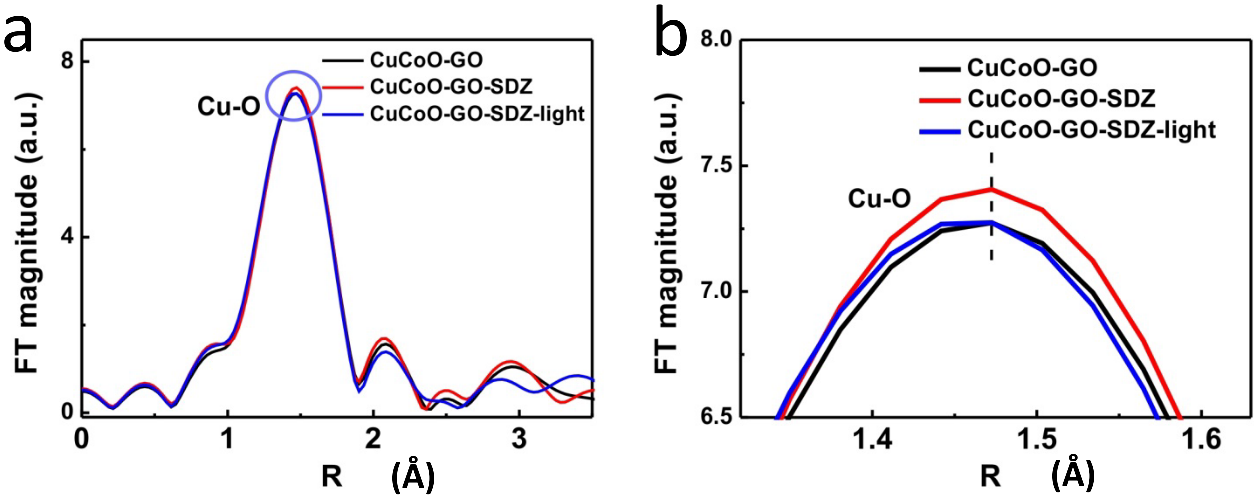
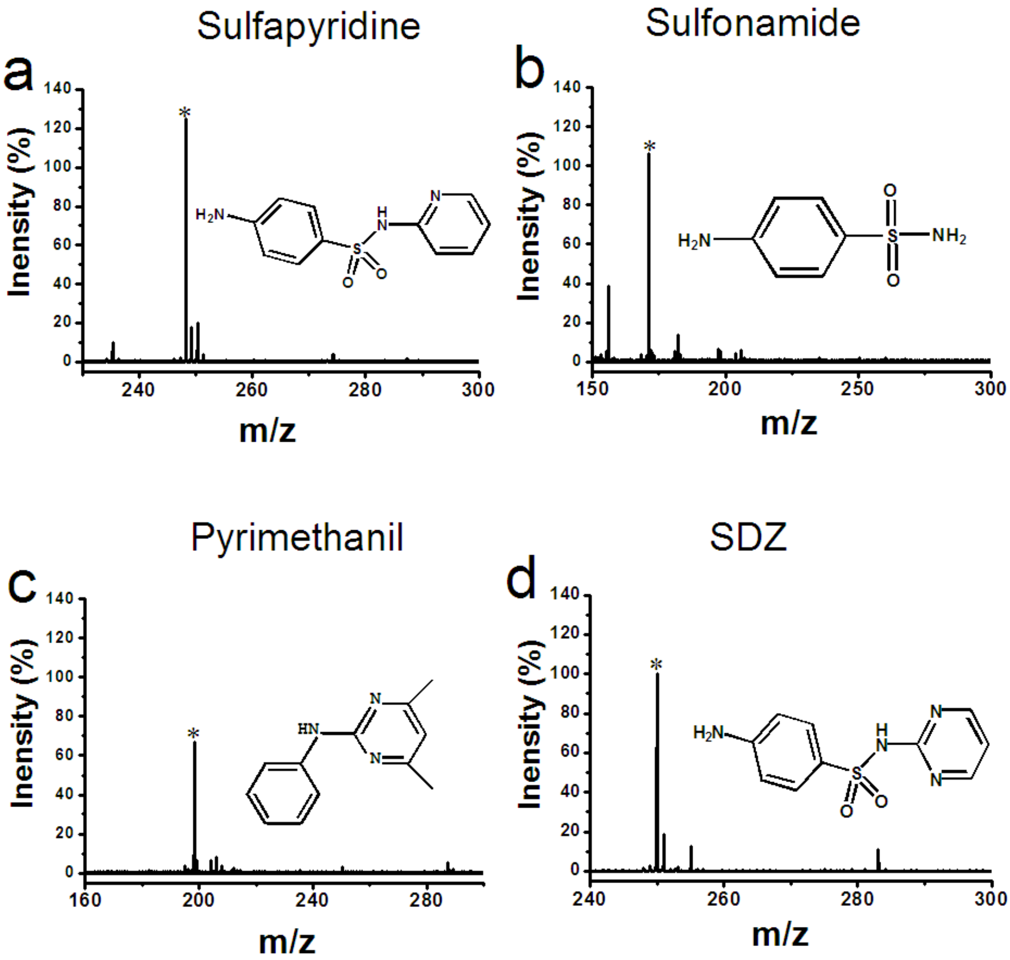


Fig. S11 (a) Fourier transform curves of the *in situ* Extended X-ray Absorption Fine Structure (EXAFS) data for CuCoO-GO at Cu K-edge. (b) Zoomed-in view of the left peak in (a).



Sulfapyridine

Sulfonamide

Pyrimethanil

SDZ

Fig. S12 Mass spectra of (a)Sulfapyridine, (b)Sulfonamide, (c) Pyrimethanil, (d) SDZ using CuCoO-GO matrix in the negative-ion mode. The laser spot size was approximately 50~100 μm. The accumulation of 3000 laser shots was applied for each spectrum.