A dielectric barrier discharge ionization based interface for online coupling surface plasmon resonance with mass spectrometry

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Electronic Supplementary Information (ESI)

In this ESI, the photo of the interface was showed in Part S-1, the modification process of the SPR sensor chip was showed in Part S-2, the result using a too small d_2 was showed in Part S-3, and the MS spectrum of analyzing acetaminophen dissolve in TBS was showed in Part S-4.

Part S-1. The operating interface

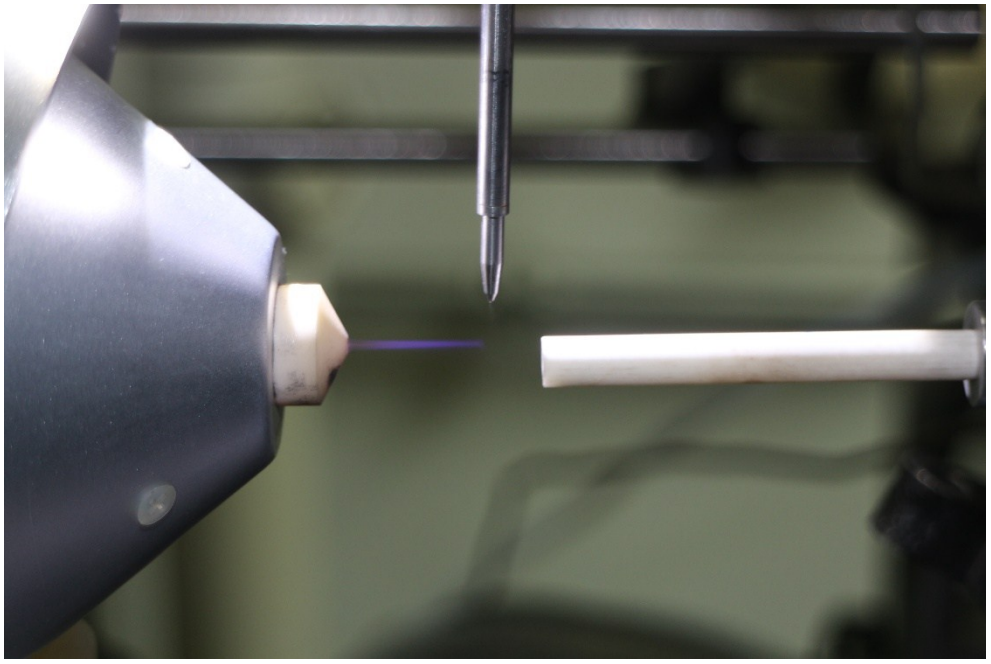

Fig. S-1 The photo of the operating interface

Part S-2. The modification of the SPR sensor chip

The sensor chip was modified with HSA by EDC/NHS coupling method. The process was showed as following.

A. Sensor chip cleaning.
   a) Blend ammonia solution, hydrogen peroxide and water with the volume ratio of 1:1:5;
   b) Immerge the sensor chip into the solution, and keep them at 90 °C for 10 min;
   c) Rinse the sensor chip with water and wait until it's dry.

B. Install the cleaned sensor chip into the SPR analyzer.

C. HSA immobilization.
   a) Inject and keep flowing 3-MPA with TCEP (4 mmol/L and 6 mmol/L) for 60 min;
   b) Inject and keep flowing EDC and NHS (0.05 g EDC and 0.01 g NHS dissolved in 4 mL H_2O) for 20 min;
   c) Inject and keep flowing HSA (0.01 g/L in CH_3COONa-CH_3COOH buffer, $c(Na^+)$ = 5 mmol/L, pH = 5.0) over night;
   d) Inject and keep flowing ethanolamine (1 mol/L, pH 8.4) for 10 min.
   e) Inject water to rinse the flow channels and the sensor chip.

After the modification of HSA onto the sensor chip, the SPR angle changed from 63.15 ° to 63.50 ° (Figure S-2), demonstrating that HSA has been successfully immobilized onto the sensor chip.

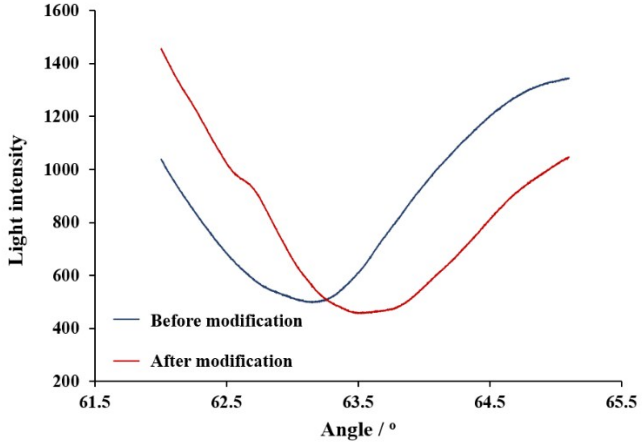

Fig. S-2 The change of the SPR angle before and after the modification with HSA

Reagents used:

3-MPA (3-mercaptopropionic acid), TCEP (tris(2-carboxyethyl)phosphine hydrochloride), EDC (N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride), NHS (N-hydroxysuccinimide) were purchased from J&K Scientific Ltd. (Beijing, China), HSA (human serum albumin was purchased from Shanghai Yuanye Biological Technology Co., Ltd. (Shanghai, China). Ethanolamine, ammonia solution, hydrogen peroxide, sodium acetate and acetic acid were analytical grade reagents.

Part S-3. Source contamination when d_2 is too small

A too small horizontal distance between the spray tip and the MS inlet (d_2) would lead to severe source contamination. Fig. S-3 showed an online SPR-MS result using approximately 1.0 mm for d_2, analyzing metronidazole dissolved in EBSS as sample solution. All other parameters were same with those mentioned in the main manuscript.

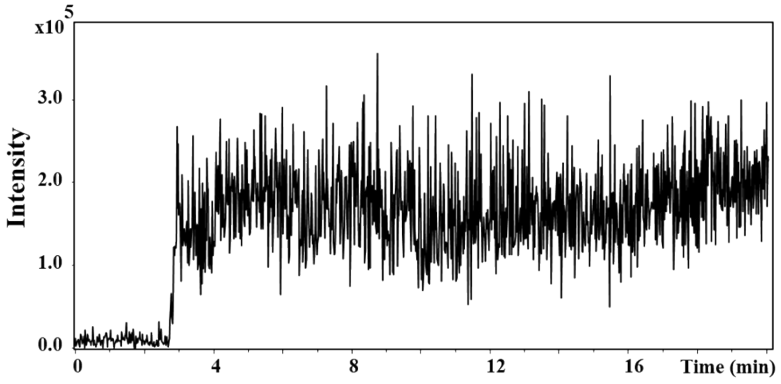

Fig. S-3 EIC of 172, a result of online SPR-MS experiment using a tip-to-MS distance (d_2) of approximately 1.0 mm. The sample was metronidazole dissolved in EBSS, all other parameters and operations were same as those used for Fig. 3 in the main manuscript.

Fig. S-3 showed that the sample signal remained high for a long time after the injection was finished at 6 min. This was because that the unionized sample solution would contaminate the MS inlet and the area near the spray tip. Using a larger d_2 would solve this problem.

Part S-4. DBDI MS spectrum of acetaminophen dissolved in TBS

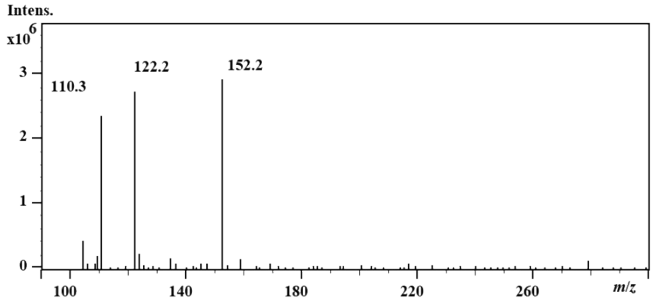

Fig. S-4 The DBDI MS spectrum of acetaminophen dissolved in TBS. The peak with *m*/*z*=122 corresponds to the tris in TBS