Electronic supplementary information

A "Switch-off" Biosensing for Chymotrypsin-Catalyzed Reaction by SPR-SERS Spectroscopy

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1. The setup of the SPR-SERS spectrometer and its working way.

The configuration of the SPR-SERS microspectrometer was reported in our previous work.[i] It is composed of three main functional parts: an incident light system, an SPR detection system and a SERS detection system.

The incident light system is mounted on one arm of a two-arm goniometer, which is comprised of a laser (532 nm, Changchun New Industries Optoelectronics Tech. Co. Ltd), two lenses (Lens 1 has a numerical aperture of 0.18 and a focal length of 25 mm, Lens 2 has a numerical aperture of 0.15 and a focal length of 10 mm) and a polarizer. The SPR detection system on the other arm of the goniometer contains Lens 3 and a photodiode. SPR data acquisition and precise angular rotation of the goniometer are both controlled via a program written by LABVIEW software (National Instruments Co.). The arms of the goniometer move with a resolution of <0.005°.

The SERS detection system consists of three parts: an inverted microscope (with a 20× object lens, NA=0.35, focal length=20.5 mm)), a CCD imaging camera with a display screen, and a spectrometer (iHR320, Jobin-Yvon Co.) with a CCD (Synapse, Jobin-Yvon Co.). A mobile mirror can switch the light to a CCD imaging camera or a spectrometer. An edge filter (λ=532nm, Semrock Inc.) was fixed on the light path to remove the Rayleigh scattering.

A semi-cylindrical prism (K9 glass with the refractive index is 1.52 at 532 nm) was fixed in the center of the goniometer. On the bottom of the prism, a 45nm thickness of silver film was modified by the vacuum evaporation deposition method. The deposition rate was 0.1nm/s. A flow cell with an injector was fixed above the silver film, which was used for the layer-by-layer assembly of analytes.

The working way of this SPR-SERS spectrometer was as follows. Two arms rotate at θ° degree in the opposite direction. When the incident angle is beyond the critical angle, the light is totally reflected at the interface of the prism/silver film. The reflected light is collected by Lens 3 and then detected by a photodiode. On the same spot of the silver film, the SERS spectra of adsorbed analytes were simultaneously excited under the evanescent field. The SERS spectra were focused into the inverted microscope and detected spectrometer. We adjusted the incident and reflected angles to obtain the angle-dependent SPR and SERS spectra.

2.XPS characterization of the surface functionalization

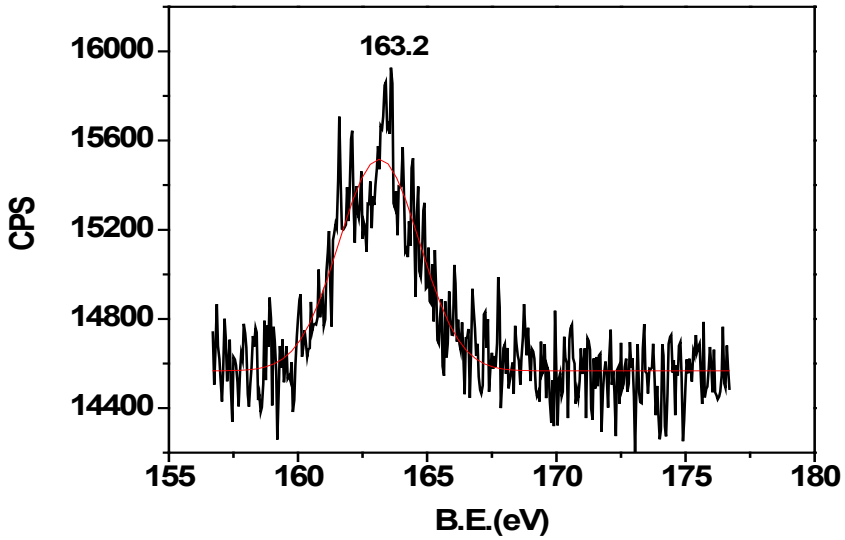

Figure S1. Single scan XPS spectra of S 2p on the surface of silver film after the assembly of peptide.

As is shown in Figure S1, before the assembly of peptide chain, the surface of the silver film did not contain compounds with the element of sulfur. The appearance of S 2p proves that the mercapto groups of the cysteine of peptide chain have been immobilized successfully on the Ag film via S–Ag bonds.

References:

[i] Liu,Y.; Xu, S. P.; Tang, B.; Wang, Y.; Zhou, J.; Zheng, X. L.; Zhao, B.; Xu, W. Q. *Rev. Sci. Instrum.* **2010**, *81*, 036105.