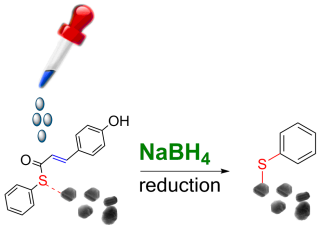

Electronic Supporting Information

In-situ SERS monitored Photoactive Yellow Protein (PYP) chromophore model elimination, nano-catalyzed phenyl redox and I_2 addition reactions

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1 Experimental Section

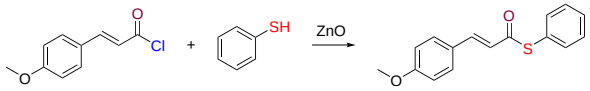
1.1 General Information

All reactions were monitored by TLC and visualized by UV lamp (254 nm). Column chromatography was performed using 200-400 mesh silica gel. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were obtained on Bruker AV-400 instrument. Chemical shifts for ^{1}H NMR spectra were reported in parts per million relative to the signal of $CDCl_3$ at 7.26 ppm. Chemical shifts for ^{13}C NMR spectra were reported in parts per million relative to the center line signal of the $CDCl_3$ triplet at 77.0 ppm. The abbreviations s, d, dd, t, q and m stand for the resonance multiplicity singlet, doublet, and doublet of doublets, triplet, quartet and multiplet, respectively. PhSCAOH crystal was obtained through test-tube solvent evaporation method, see Figure 11. In detail, test-tube contained PhSCAOH (30 mg) in 5 mL THF solution was placed in the open air for 7 days. Yellow crystal was obtained and filtered with filter paper.Filter paper was used here for two reasons, first, filter paper could hold crystal samples, second filter paper dried the mother liquid on the crystal surface, see Figure 11. Crystal data was collected on Bruker Smart Apex-II X-Ray Diffractometer Instrument.

The SERS/solid-state Raman spectra were recorded on Renishaw inVia Raman microscope system with spatial resolution 0.1 μm, laser spot diameter is 1 μm with integration time 1 s, controlled through the WiRE 3.4 software. Leica lens magnification 50 $\times$ objective was applied through out the experiments. Sample images were taken on Leica camera. The incident laser power 3 mW (633 nm, 100% power), 10% power (0.3 mW, 633 nmp) was applied for the 100% (3 mW) would cause sample carbonization, see Figure 9. In order to get the reliable spectrum results, all experiments repeated at least three times.

Thin layer chromatography (TLC) was used to develop and distribute the PhSCAOH on the TLC plate. The spot developed was spayed with Ag sol, and it was dried in the open air before SERS spectra acquisitions. PhSCAOH/Benzenethiol (PhSH, AR) SERS spectra were recorded on the TLC plate with Ag/Au NPs sprayed. TLC plates was used as SERS substrate. Randomly selected three different area were recorded to give reliable results. SERS mapping was carried out within the randomly selected area, at least 50 spectra were collected to give reliable results. The PhSCAOH crystalline sample was place between two glass slides and crushed into small particles, then the crystalline samples was mounted on the Renishaw inVia Raman system. PhSCAOH solid sample Raman spectra were acquired, see Figure 4.

1.2 Preparation of PhSCAOH



S-phenyl (E)-3-(4-methoxyphenyl)prop-2-enethioate (PhSCAOMe) To a stirred mixture of 4-Methoxycinnamoyl chloride (0.98g, 5 mmol) and zinc oxide powder (0.21g, 2.5 mmol) in 5 mL dichloromethane (DCM), thiol (0.55g, 5 mmol) was added. The mixture was stirred overnight. Then zinc oxide was filtered off through a buchuer funnel, and washed with DCM (3×5 mL). The extract was washed with aqueous Na_2CO_3 3 times and dried over anhydrous Na_2SO_4, The solution was concentrated in vacuum and purified by column chromatography, see Figure 10. using petroleum ether/ethyl acetate (1:10) as eluent to afford white solid 1 (1.02g, 76%).

S-phenyl (E)-3-(4-hydroxyphenyl)prop-2-enethioate (PhSCAOH) 0.54 g of PhSCAOMe and 5 ml DCM were added in 25 ml bottom flask cooled to -20°C, then 0.38 ml boron tribromide (BBr_3) (1 g, 0.4 mmol) was syringed. The reaction mixture was stirred 5 h and quenched by saturated $NaHCO_3$ solution. The mixture was extracted by DCM (3×5 mL), washed by brine and dried over anhydrous Na_2SO_4, The solvent was evaporated *in vacuo* and the residue was purified by silica gel column chromatography (Figure 10) using petroleum ether/ethyl acetate (1:1) as eluent to give yellow solid PhSCAOH (0.42 g, 82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 15.7 Hz, 1H), 7.55-7.40 (m, 7H), 6.84 (dd, J = 7.5, 4.9 Hz, 2H), 6.66 (d, J = 15.7 Hz, 1H). ^{13}C NMR (101 MHz, CDCl3) δ 188.39,

158.18, 141.43, 134.67, 130.51, 129.40, 129.18, 127.75, 126.75, 121.73, 116.03.

2 Figures

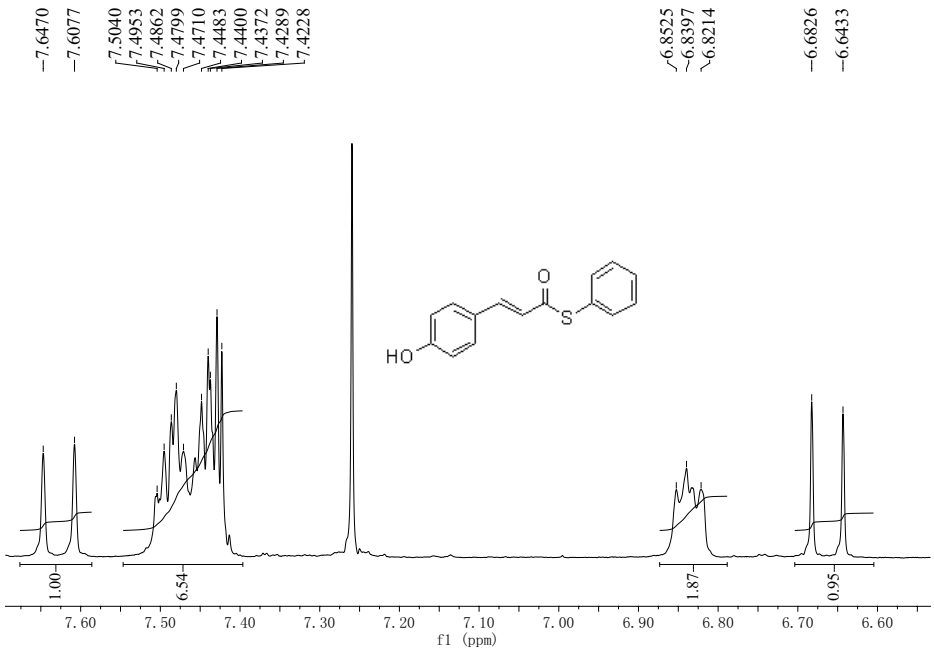


Figure 1 PhSCAOH ^{1}H NMR.

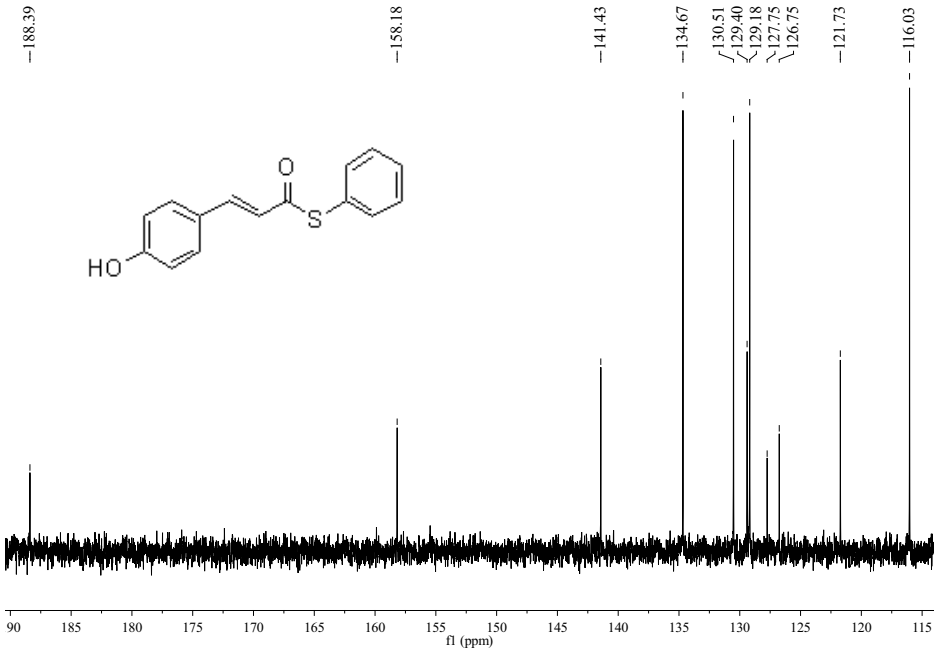


Figure 2 PhSCAOH ^{13}C NMR.

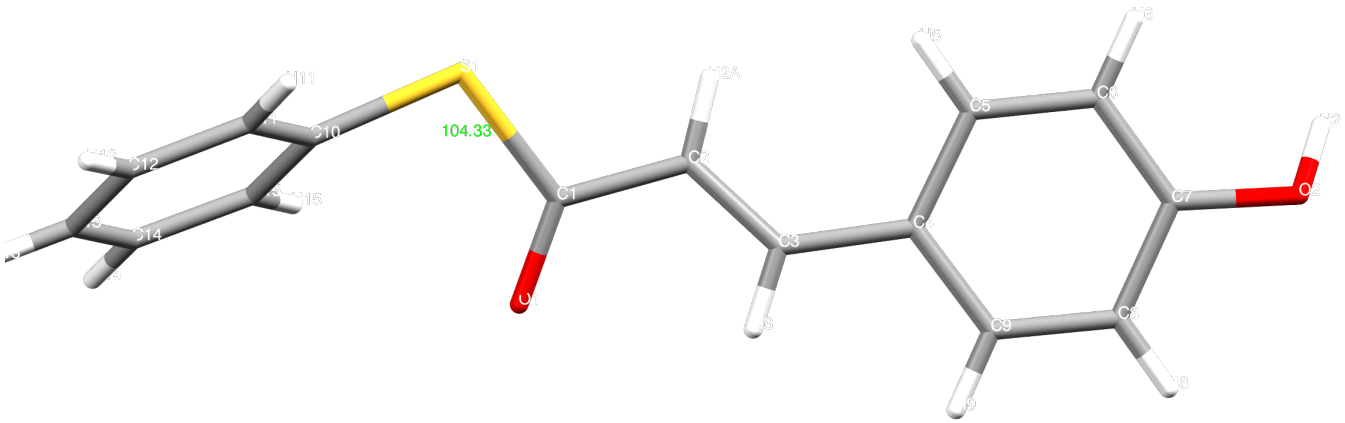


Figure 3 PhSCAOH crystal structure.

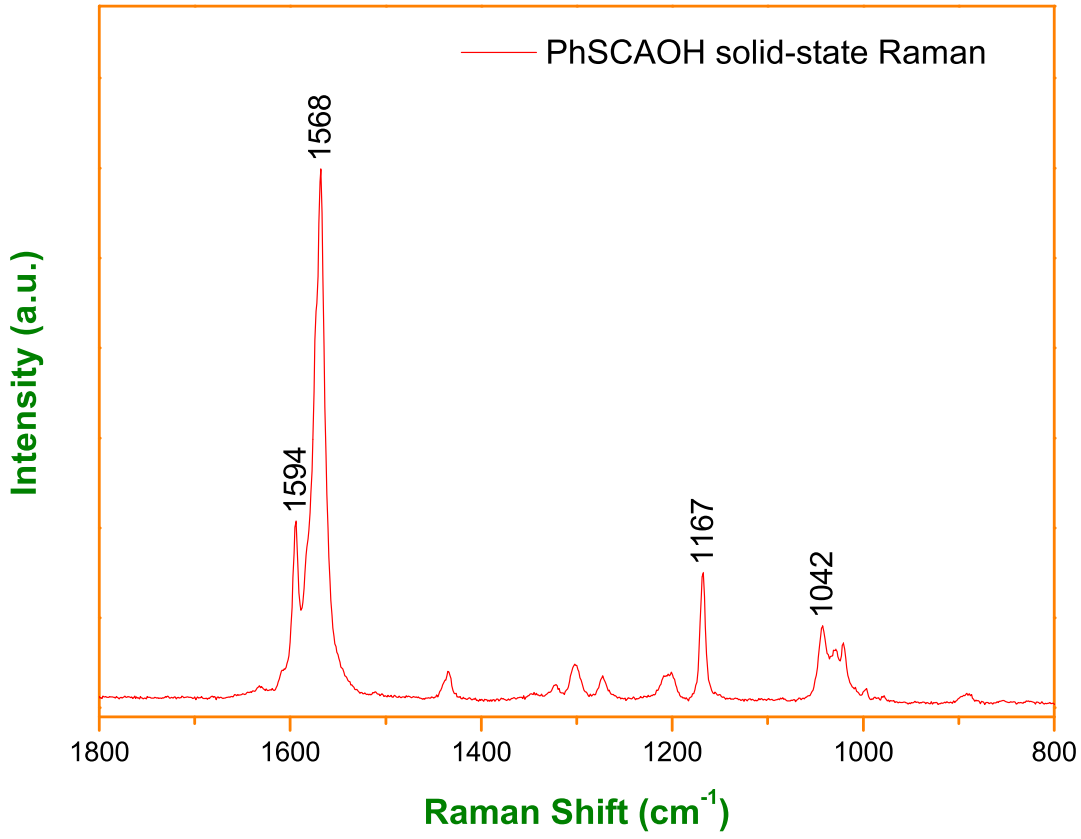


Figure 4 Solid state Raman spectra of PhSCAOH.

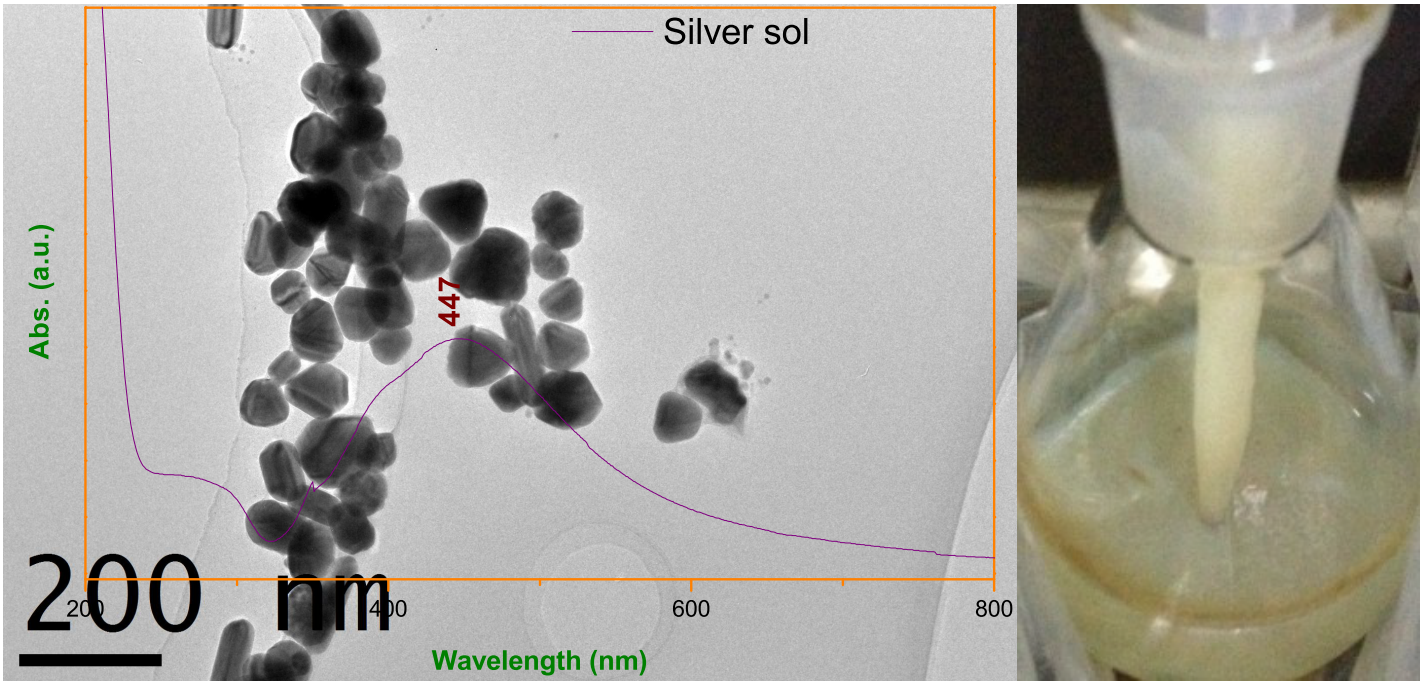


Figure 5 Ag sol TEM image and UV-vis spectra.

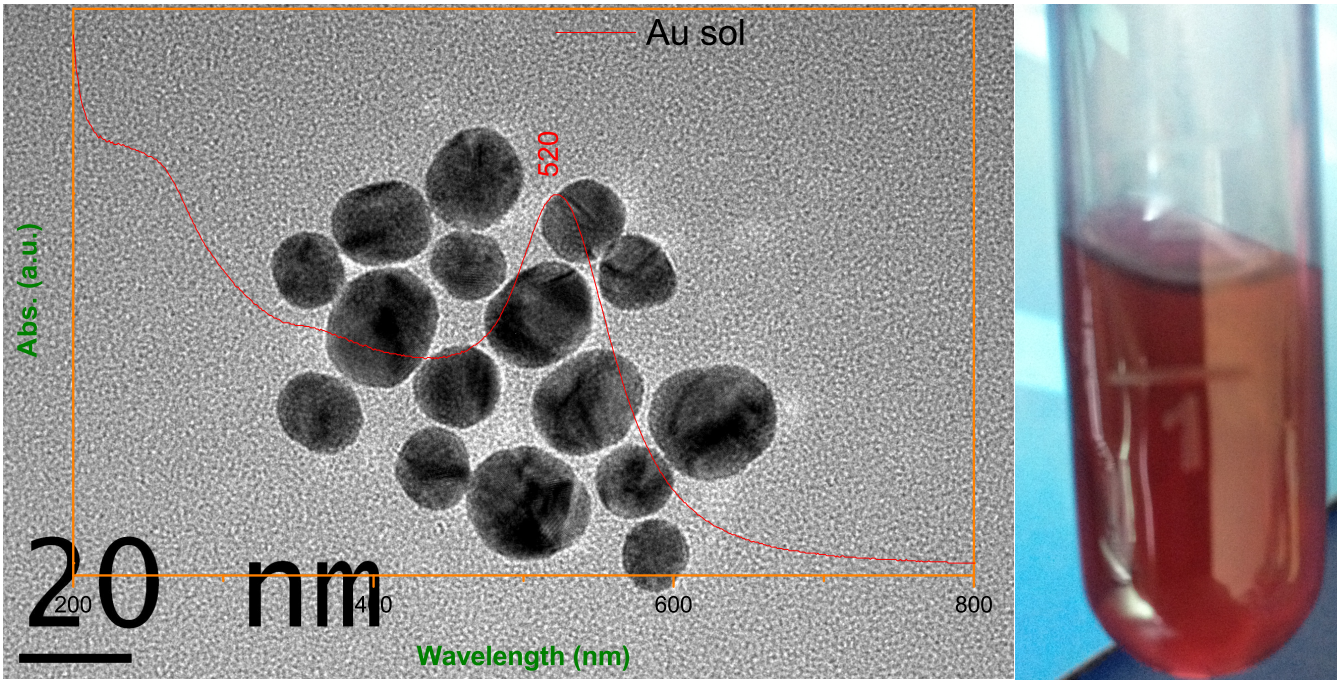


Figure 6 Au sol TEM image and UV-vis spectra.

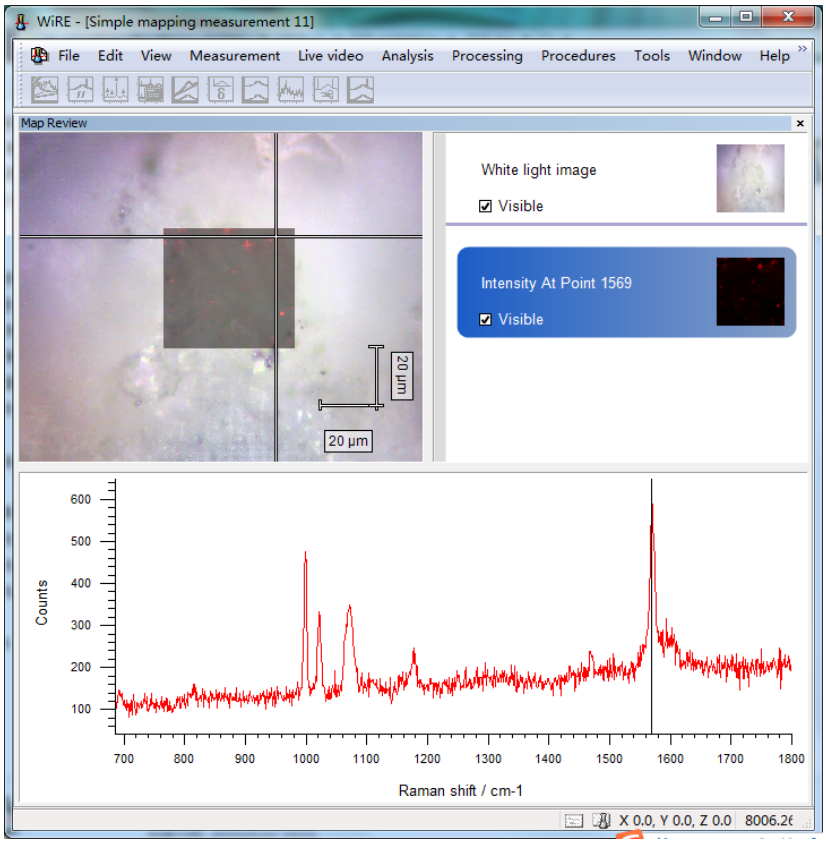


Figure 7 SERS intensities depressed.

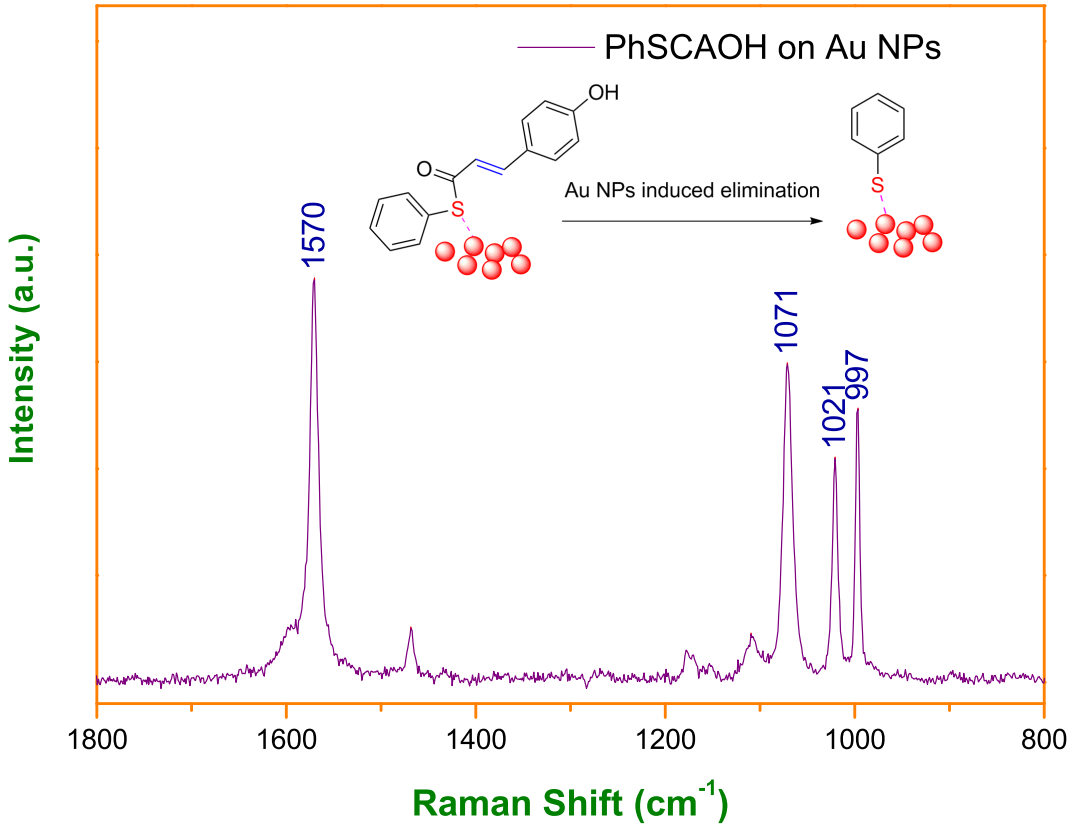


Figure 8 SERS spectra of PhSCAOH on Au NPs' surface.

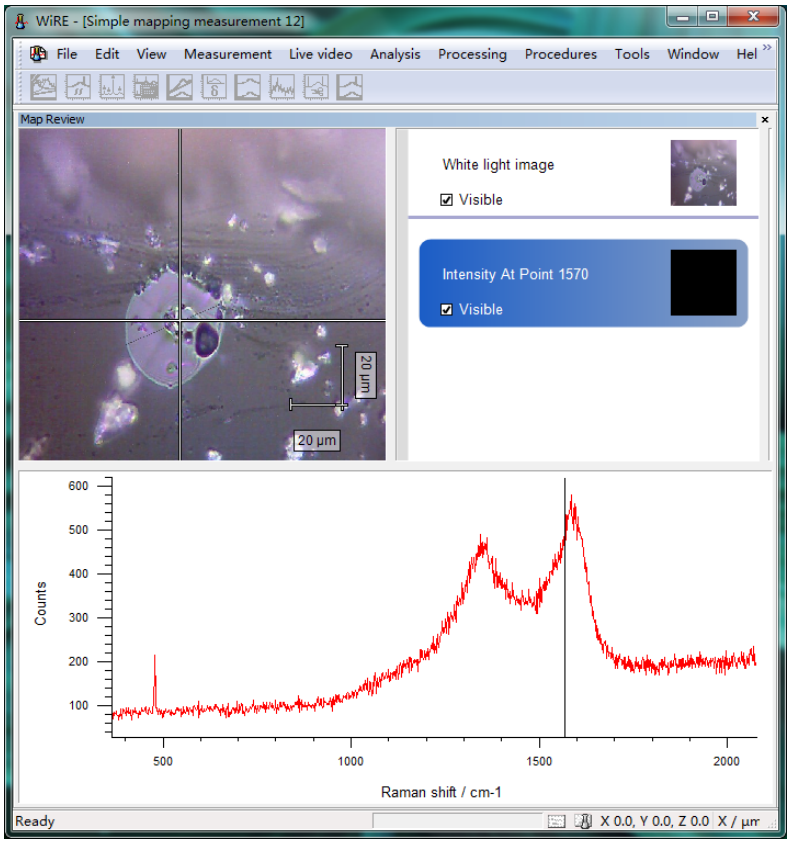


Figure 9 633 nm laser 100% power (3 mW) with exposure time 1 s caused carbonization.

Figure 10 PhSCAOH was purified through column chromatography.

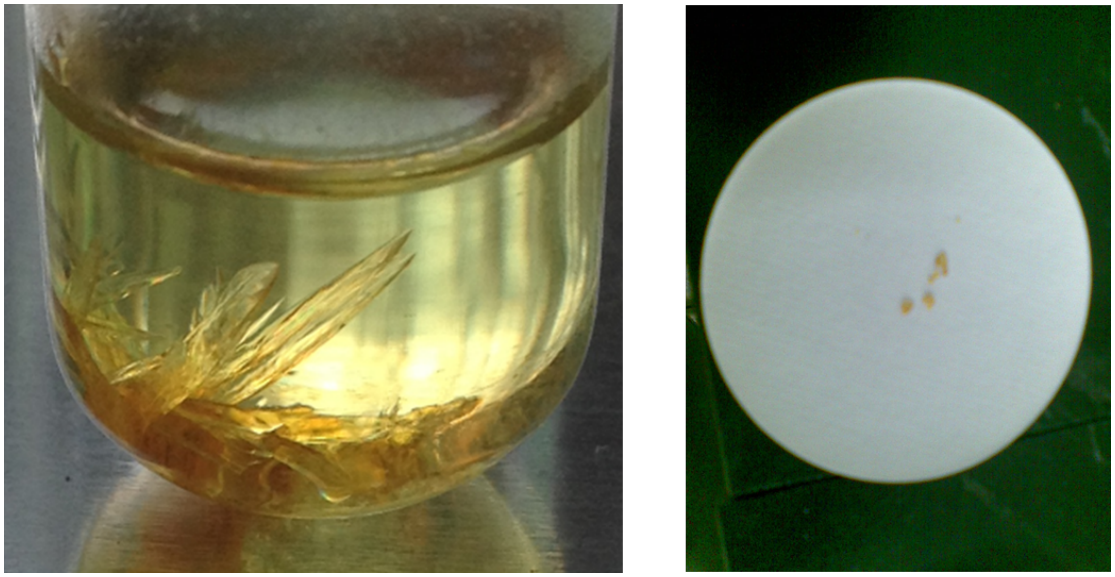


Figure 11 Filter paper is used for crystal surface solvent drying.