

**Highly efficient photo-induced enhanced Raman spectroscopy (PIERS) from plasmonic nanoparticles decorated 3D semiconductor arrays for ultrasensitive, portable and recyclable detection of organic pollutants**

Maofeng Zhang, <sup>\*a</sup> Haoran Sun, <sup>b</sup> Xin Chen, <sup>b</sup> Jian Yang, <sup>b</sup> Liang Shi <sup>c</sup> Tun Chen, <sup>b</sup> Zhiyong Bao, <sup>b</sup> Jiaqin Liu, <sup>\*d</sup> and Yucheng Wu <sup>b</sup>

*a. School of Chemistry and Chemical Engineering, Hefei University of Technology, 193 Tunxi Road, Hefei, 230009, China*

*b. School of Materials Science and Engineering, Hefei University of Technology, 193 Tunxi Road, Hefei, 230009, China*

*c. Department of Chemistry, University of Science and Technology of China, 96 Jinzhai Road, Hefei, 230026, China*

*d. Institute of Industry and Equipment Technology, Hefei University of Technology, 193 Tunxi Road, Hefei, 230009, China*

\*E-mail: mfzhang@hfut.edu.cn, Tel: +86 18019595355

\*E-mail: jqliu@hfut.edu.cn, Tel: +86 13866186310

### **Synthesis of TiO<sub>2</sub> nanosheets array**

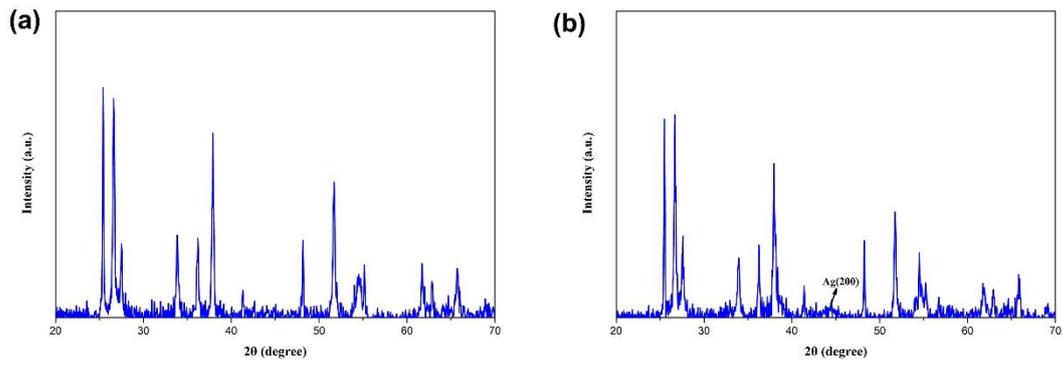
The anatase TiO<sub>2</sub> nanosheets array was synthesized on fluorine-doped tin oxide (FTO) glass substrates by a controllable hydrothermal method. Briefly, a mixture of deionized water (17.5 mL) and hydrochloric acid (36.0% ~ 38.0% by weight, 12.5 mL) was added to a Teflon-lined stainless-steel autoclave (50 mL volume) and stirred for 10 min by magnetic stirring apparatus. Then 0.5 mL tetrabutyl titanate (98.0 % purity) and 0.3 g ammonium hexafluorotitanate (98.0% purity) were added into the solution in turn and stirred for another 10 min. Then, a piece of FTO substrate (transmittance  $\geq 80\%$ , sheet resistivity  $\leq 7 \Omega/\square$ ), ultrasonically cleaned in turn by toluene, acetone, ethanol, and deionized water for 20 min each before, was placed against the wall of the liner with working face up. The hydrothermal synthesis was maintained at 150 °C for 7 ~ 9 h in an oven. After cooling down to room temperature, the FTO with TiO<sub>2</sub> nanosheets was rinsed with deionized water thoroughly and dried in air. Then the sample was annealed at 500 °C for 2 h in a tube furnace. Here, the sample of anatase TiO<sub>2</sub> nanosheets on FTO substrate was labeled as T0.

### **Synthesis of pure AgNPs**

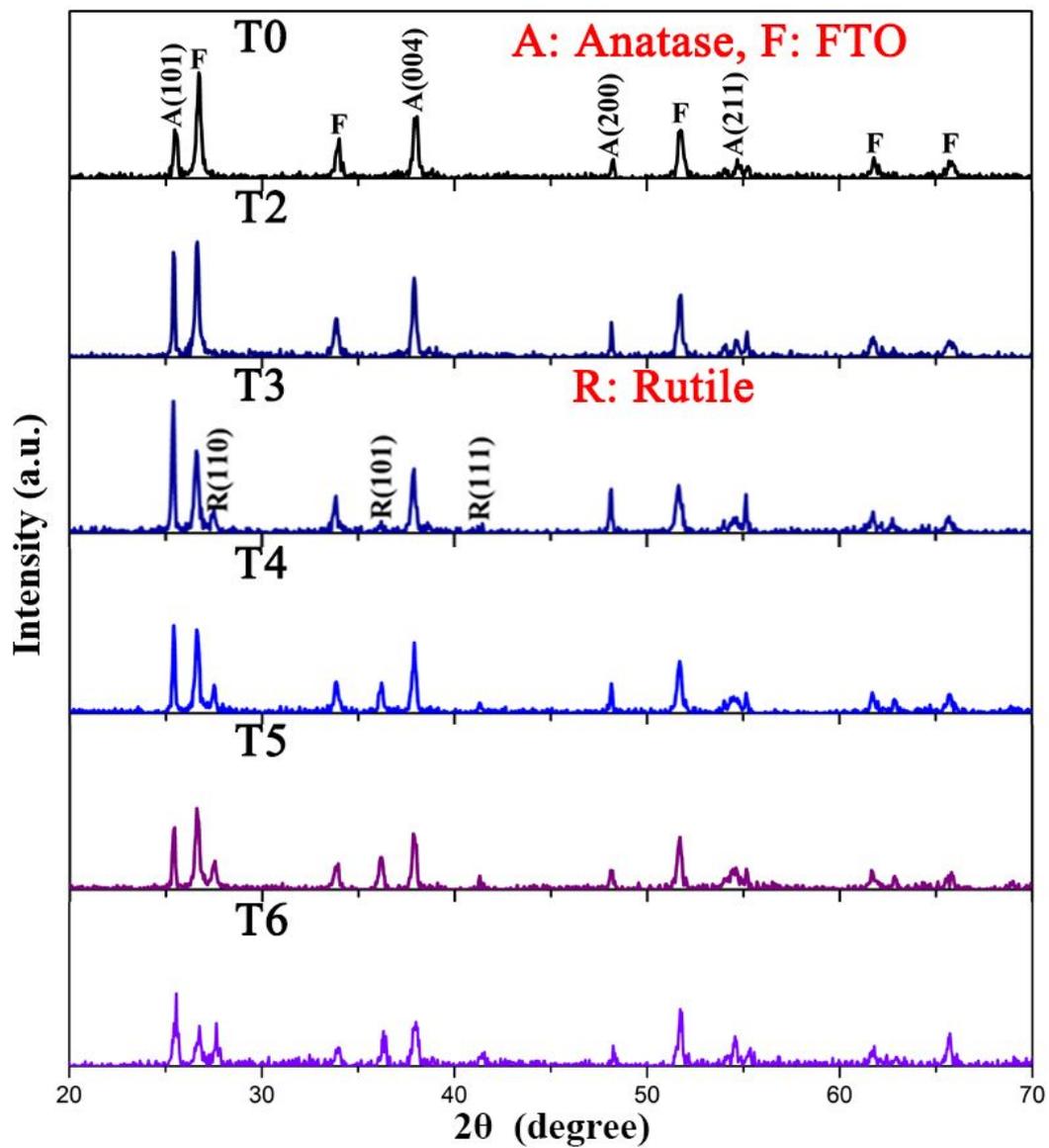
Firstly, 0.50 g PVP was added into 35 ml ethanol, which was stirred with magnetic stirrer, and then 0.17 g AgNO<sub>3</sub> was added during stirring. The mixture was transferred into an autoclave lined with Teflon (Total volume is 50 mL) and was heated to 100 °C for 20 h. After the autoclave was cooled to room temperature, the AgNPs was separated by centrifugation and washed successively with ethanol and deionized water, and kept in deionized water for further use.

### **Calculation of the ratio of TiO<sub>2</sub> and Ag in the composite**

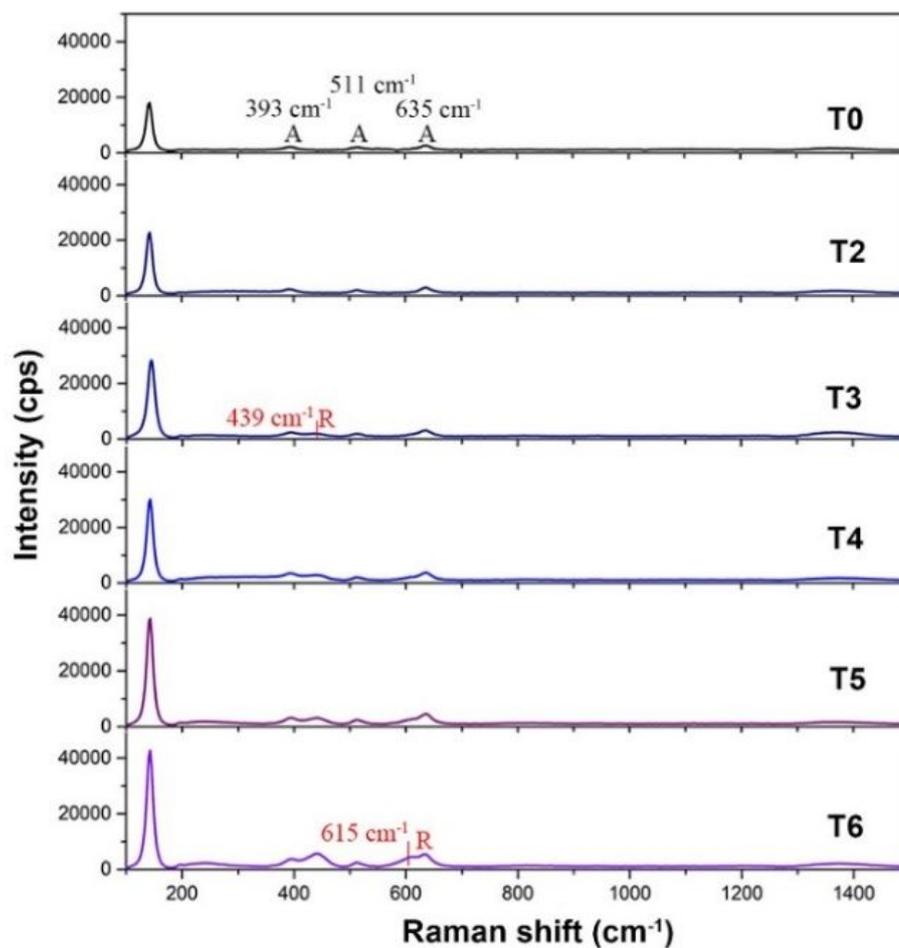
The original FTO substrate, FTO-TiO<sub>2</sub> substrate and FTO-TiO<sub>2</sub>-Ag substrate were weighed respectively. By comparing the increase in mass, we obtained the mass of the anatase TiO<sub>2</sub> was 0.0179 g, anatase/rutile TiO<sub>2</sub>-hybird was 0.0341g and that of AgNPs was 0.0033g. Hence, we can easily calculate the mass ratio of TiO<sub>2</sub> and Ag in the composite is about 10.3 : 1.



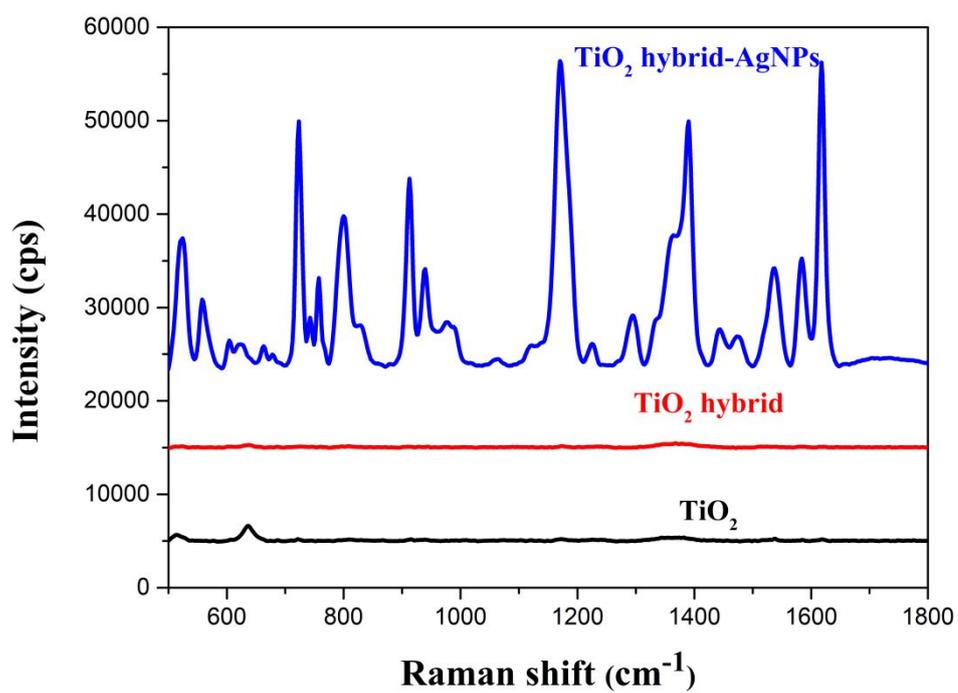
**Figure S1.** XRD patterns of anatase/rutile  $\text{TiO}_2$  heterostructure before (a) and after (b) AgNPs deposition.



**Figure S2.** XRD patterns of the TiO<sub>2</sub> samples obtained during the second hydrothermal reaction times: 0 hour (T0), 2 hours (T2), 3 hours (T3), 4 hours (T4), 5 hours (T5) and 6 hours (T6).



**Figure S3.** Raman spectra of the TiO<sub>2</sub> samples obtained during the second hydrothermal reaction times: 0 hour (T0), 2 hours (T2), 3 hours (T3), 4 hours (T4), 5 hours (T5) and 6 hours (T6).

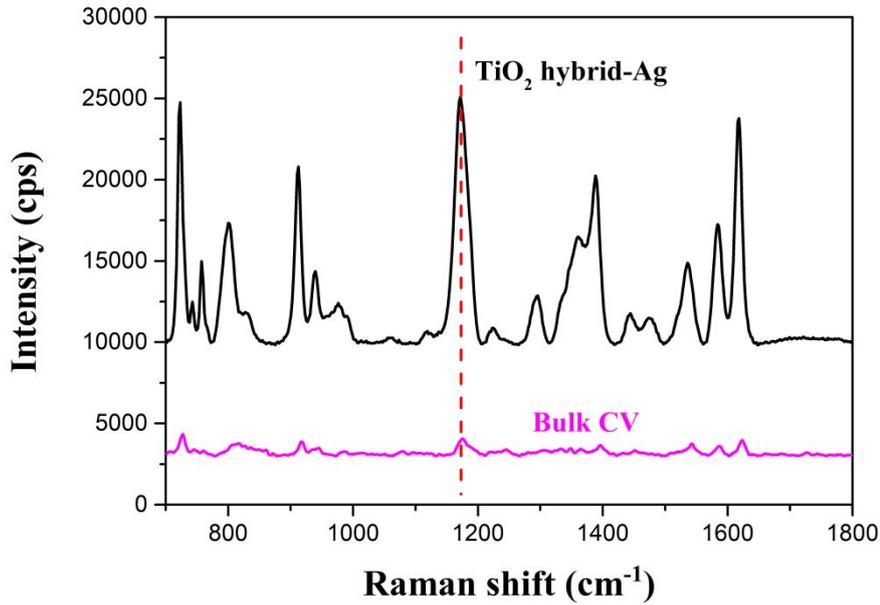


**Figure S4.** Raman spectra obtained from anatase TiO<sub>2</sub> substrate, TiO<sub>2</sub> hybrid substrate and TiO<sub>2</sub> hybrid-AgNPs absorbed on CV (10<sup>-3</sup> M) solution.

**Table S1.** Reference values for enhancement calculation from TiO<sub>2</sub> heterostructure-AgNPs substrates with and without UV irradiation.

<b>Analyte</b>	<b>Peak position (cm<sup>-1</sup>)</b>	<b>SERS intensity (cps)</b>	<b>PIERS intensity (cps)</b>	<b>Enhancement magnitude</b>
<b>MG</b>	1620	410.5 ± 41.5	8182 ± 463	20.0
<b>CV</b>	1174	221.5 ± 30.5	3043 ± 191	13.7
<b>R6G</b>	1508	492.2 ± 86.0	7313 ± 431	14.9
<b>Thiram</b>	1380	132.5 ± 21.0	3680 ± 331	27.8
<b>Acephate</b>	675	387.0 ± 69.5	5660 ± 415	14.6

## Calculation of Enhancement factor (EF)



**Figure S5.** Raman spectra obtained from bulk CV ( $10^{-2}$  M) and TiO<sub>2</sub> hybrid-Ag with CV ( $10^{-6}$  M) as analytes.

$$EF = (I_{SERS}/I_{BULK}) \times (N_{BULK}/N_{SERS})$$

$$N_{BULK} = (\text{Laser spot area}/\text{Diffusion area}) \times (N_A \times V_{BULK} \times C_{BULK})$$

$$N_{SERS} = (\text{Laser spot area}/\text{Substrate area}) \times (N_A \times V_{SERS} \times C_{SERS})$$

$$\text{Diffusion area} = \pi(d/2)^2 = 0.5027 \text{ cm}^2$$

$$\text{Substrate area} = 0.25 \text{ cm}^2$$

$$V_{BULK} = V_{SERS}$$

$$C_{BULK} = 10^4 \times C_{SERS}$$

$$N_{BULK} / N_{SERS} = (0.25/0.5027) \times 10^5 = 5 \times 10^4$$

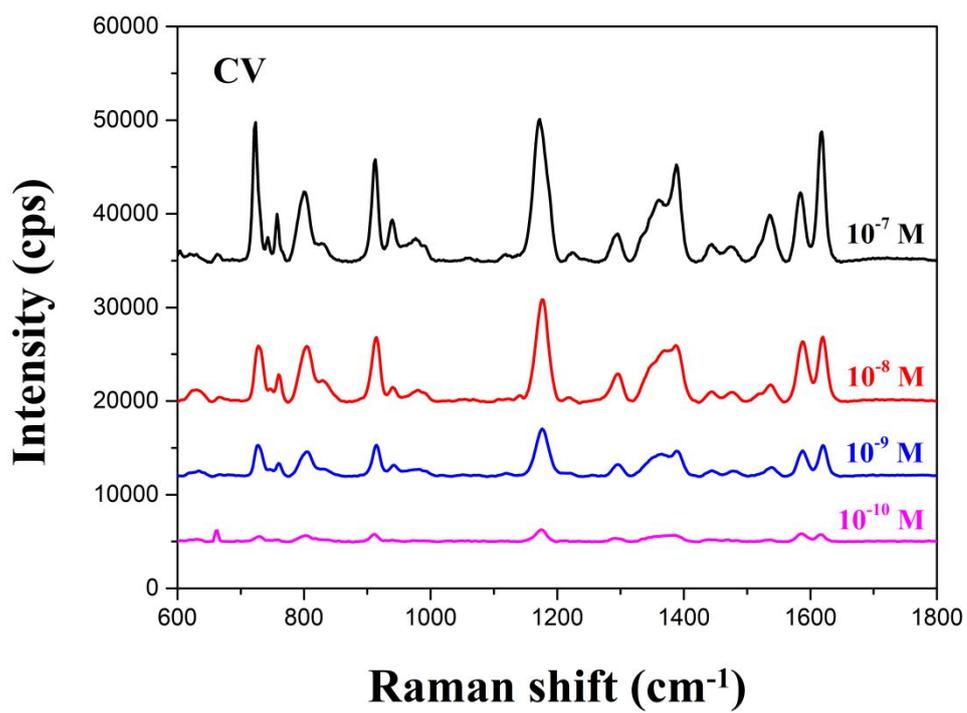
I = intensity of the 1174 cm<sup>-1</sup> peak

$$I_{BULK} = 25405 \text{ cps}$$

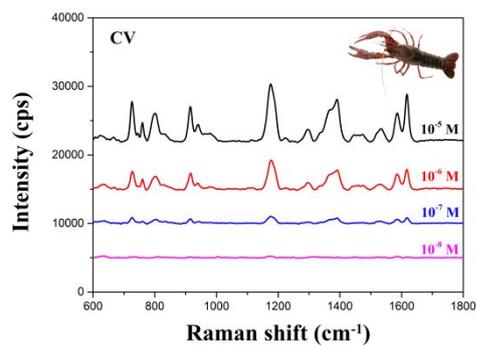
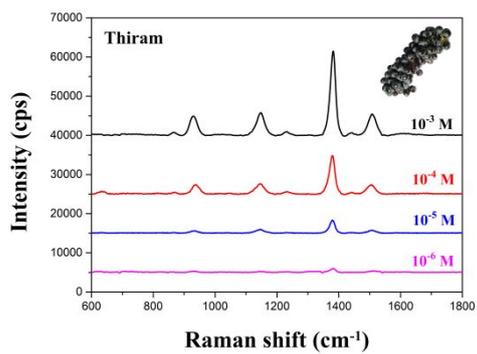
$$I_{SERS} = 404222 \text{ cps}$$

$$I_{SERS} / I_{BULK} = 15.9$$

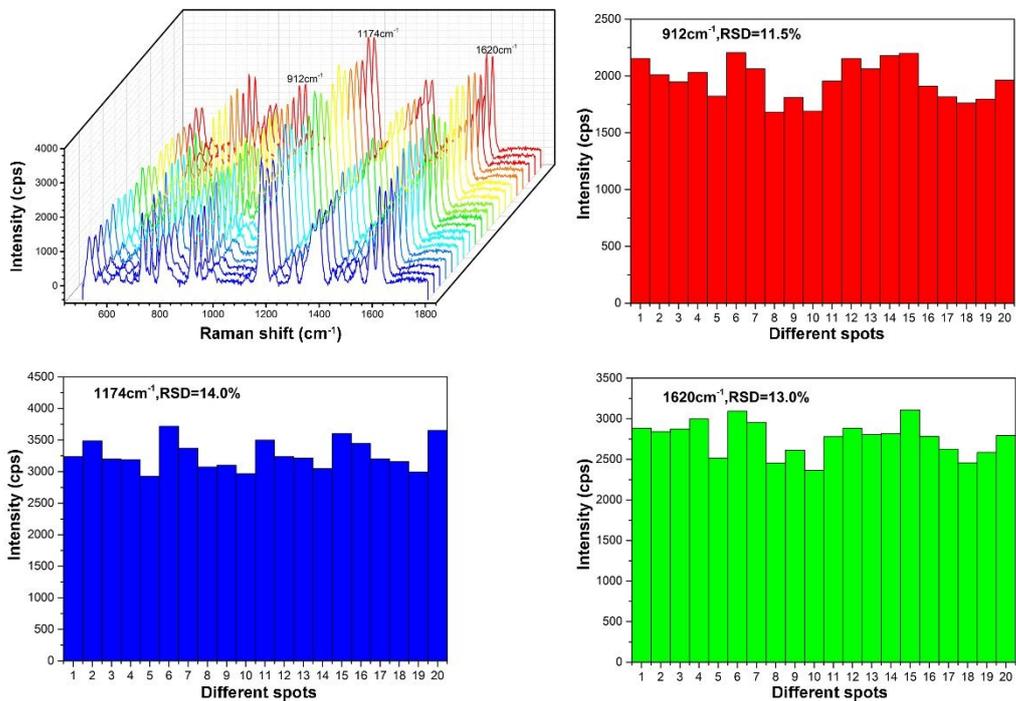
$$EF = (I_{SERS} / I_{BULK}) \times (N_{BULK} / N_{SERS}) = 7.95 \times 10^5$$



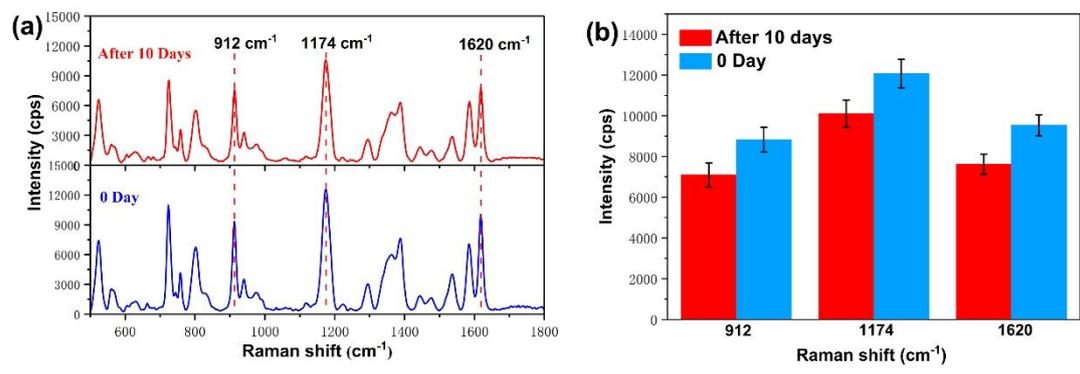
**Figure S6.** SERS spectra of CV measured by the PIERS-based sensor.



**Figure S7.** SERS detection of thiram residues on grapes surface and CV drug residues on lobster surface.



**Figure S8.** SERS spectra of CV ( $10^{-7}$  M) absorbed on  $\text{TiO}_2$  heterostructure-AgNPs substrates, 20 spots were randomly measured for calculation of RSD values of peaks at 912, 1174, and 1620  $\text{cm}^{-1}$ .



**Figure S9.** Stability tests of CV absorbed on TiO<sub>2</sub>-AgNPs substrates with rutile content of 35.3 % before and after storing in air for 10 days.