Electronic Supplementary Material (ESI) for Analyst.


Electronic Supporting Information

# Label-free selective SERS detection of PCB77 using DNA aptamer modified $SiO_2$@Au core–shell nanoparticles

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## The Supporting Information includes:

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## Part S1 Experimental section

### Preparation of SERS-active $SiO_2$@Au core/shell NPs

At first，the silica nanoparticles were prepared. For this purpose, ammonium solution (30 wt%) of 3 mL was mixed with 50 mL ethanol, and 1.5 mL TEOS was added, and then the solution was smoothly stirred overnight. An excess of APTMS (200 μL) was then added to the prepared silica nanoparticles solution (10 mL), and the solution was slowly stirred overnight. To enhance the covalent bonding of APTMS with the surface of silica, the mixed solution was gently heated at 75℃ for 2h, and ethanol was added continuously to keep the total volume of solution constant. APTMS modified silica nanoparticles were washed using ethanol three times by centrifugation and ultrasonication and dispersed into pure ethanol (6 mL).

Next, the 1-3 nm gold seeds were prepared. To prepare the gold seeds of 1-3 nm, 0.5 mL of 1.0 M NaOH was added to 45 mL of ultrapure water, followed by the addition of 1.0 mL THPC (50 mmol/L aqueous solution). The mixed solution was stirred for 5 min and then 36 μL of 1.0 M $HAuCl_4 3H_2O$ was added. The color of solution immediately turned to brown. After 15 min of stirring, the solution was stored at 4℃ for one week.

Then, addition of the APTMS modified silica nanoparticles (150 μL) to the undiluted gold seeds solution (12 mL) led to the residence of gold seeds onto the surface of silica. The mixed solution was gently shaken by hand for 10 min and kept without interruption for 12h. The silica-gold seeds colloids were washed by ethanol and water successively and dispersed into ultrapure water (4 mL).

At last, in a reaction flask, 25 mg $K_2CO_3$ was added into 100 mL ultrapure water

with stirring for 10 min, followed by adding of 36 μL of 1.0 M $HAuCl_4 3H_2O$. The solution turned out to be colorless in 30 min and the mixture was aged for three days before using. The colloid containing silica-gold seeds (150 μL) was injected to 10 mL of the colorless solution under vigorously stirring and 10 μL of formaldehyde was added immediately. The mixture's color changed gradually from firstly purple to blue and then to green in 30 min, and the reaction of solution was finally stopped through centrifugation. The final $SiO_2$@Au core/shell NPs were dispersed in ultrapure water (6 mL) for long time storage.

**Immobilzation of $SiO_2$@Au core/shell NPs on quartz slides**

Quartz glass was chosen as the supporting basement because of its low interference. The quartz slides were first submerged in a fresh prepared piranha solution ($H_2SO_4$:$H_2O_2$=3:1) for 2h at 80℃, and then rinsed with dry ethanol and ultrapure water, and dried with nitrogen gas flow. Then the quartz slides were submerged in a 20mL solution of APTMS (1 μL of APTMS per 1mL water) for 15 min, and then were removed from the APTMS solution, rinsed with ethanol and water, dried with nitrogen gas flow. The quartz slides were submerged in an concentrated Au nanoshell suspension overnight. The $SiO_2$@Au core/shell NPs were distributed homogeneously on the quartz slide through self-assembly.

**Characterization of the nanoparticles**

The freshly synthesized $SiO_2$@Au core/shell NPs were characterized by using scanning electron microscope (SEM), transmission electron microscope (TEM) and UV-vis spectrophotometer. SEM images were obtained using a Hitach S-4800 scanning electron microscope. TEM experiments were carried out with a JEOL 2010 microscope operated at an accelerating voltage of 100 kV. The samples were dissolved in ethanol dropped on copper grids. UV-vis spectroscopy was performed on SHIMADZH, UV-2550 spectrophotometer with a spectral range from 800 to 200 nm.

As shown in Fig. S1a, the core-shell structure was complete and the diameter of nanoparticles was uniform. The diameter of silica particles used in our experiment was about 100 nm and the composite particle size was 120 nm in diameter. So, the Au shell thickness was estimated about 20 nm. Fig. S1b shows that the surface plasmon

resonance (SPR) peak of the $SiO_2$@Au core/shell NPs is about at 750 nm, and optimized SERS effect can be obtained due to electromagnetic enhancement (EM) mechanism. The TEM picture of single $SiO_2$@Au core/shell nanoparticle and confirms that a gold thin film is formed on the surface of the silica nanoparticle.

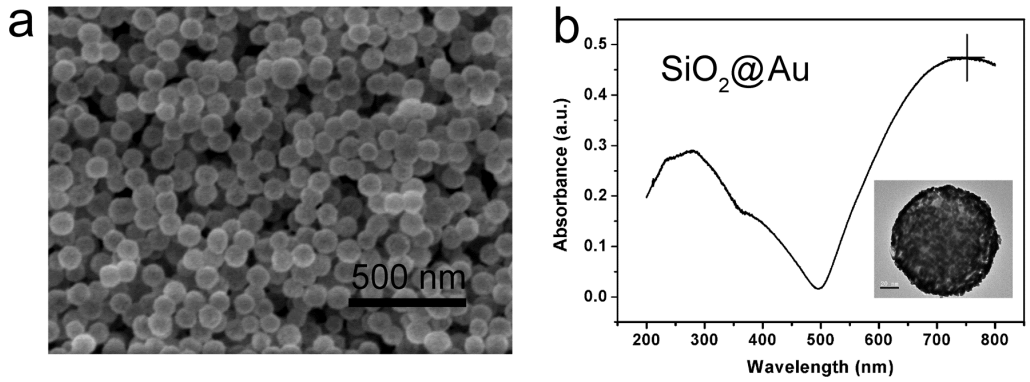


**Fig. S1**. a:The SEM picture of $SiO_2$@Au core/shell NPs, and the diameter of these nanoparticles were about 120 nm. b:UV/Vis spectra of $SiO_2$@Au core/shell NPs, and the inset graph was the TEM picture of single $SiO_2$@Au core/shell nanoparticle.

**Fabrication of aptamer modified SERS substrate**

The thiol-modified oligonucleotide was incubated in 10 mM triscarboxyethylphosphine (TCEP) in TE at pH 7.4 for 2h at room temperature, and then desalted through NAP-5 (GE healthcare) to remove excess TCEP and ionic compound. The final concentration of ssDNA was 20 μM determined by absorption spectroscopy at 260 nm. The purified DNA was then heated to 90℃ for 10 min in water bath and then cooled in ice bath immediately. 5 μL pretreated ssDNA water solution was dropped on the freshly prepared substrate under wet condition at 4℃. The samples were kept in fridge overnight.

The ssDNA modified substrates were rinsed with pure water to remove unbounded ssDNA and dried with flow of nitrogen gas. The substrates were then immersed in 10 nM MCH water solution for 4h, with MCH working as a spacer to remove the non-covalently attached ssDNA and avoided the molecules absorbed on

metal surface directly. Finally, the substrates were rinsed with pure water several times and dried with nitrogen gas flow.

**The influence of DMSO in this label-free detection biosensor system**

In this detection system, PCBs could be dissolved in DMSO water solution considering the low solubility of PCBs in water. The influence of DMSO must be corrected during SERS spectra recording, which has a obvious SERS band at 672 $cm^{-1}$ shown in Fig. S3. This band may introduce the interference to the band at 660 $cm^{-1}$ assigned to the breathing vibration mode of guanine[1]. Pemberton et al.[2] have studied the orientation of DMSO on the interface of Ag electrodes through SERS and the band at 671 $cm^{-1}$ was attributed to C-S-C vibration. Interestingly, when the DMSO treated substrates were washed with large amount of pure water several times, the SERS intensity of 672 $cm^{-1}$ decreased rapidly and the SERS intensity of 736 $cm^{-1}$ (attributed to the ring breathing mode of adenine) recovered. This phenomenon suggests that DMSO can be detached by flowing water and the influence of Raman recording can be avoided. To minimize the influence of the DMSO, the concentration of DMSO was used as low as 5% (V/V).

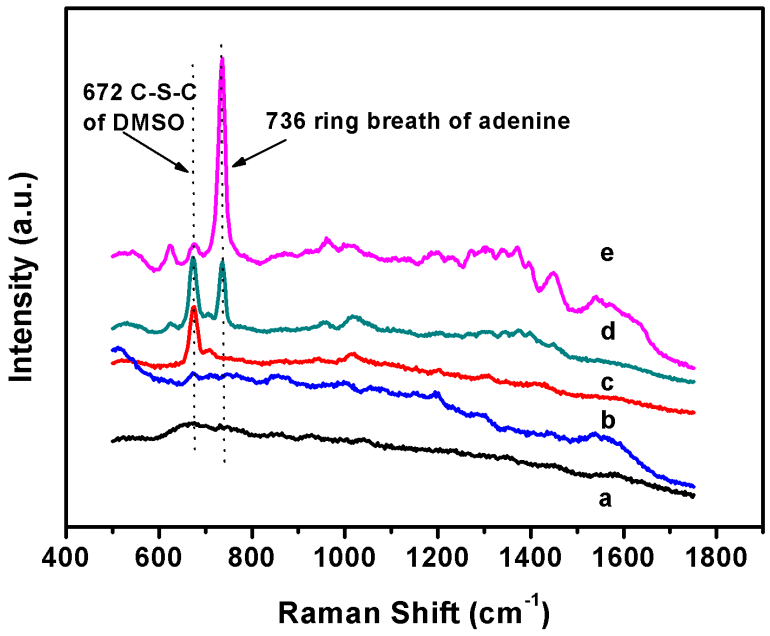


**Fig. S2**. a: background b:DMSO washed c: DMSO unwashed d:adenine+DMSO unwashed e:adenine+DMSO washed

**The influence of MCH during Raman recording**

In this sensing system, MCH was chosen to block the residual active sites after binding DNA on the surface of Au shells. It can avoid nonspecific adsorption of ssDNA. As shown in Fig. S3, with decrease of concentration of MCH, the band at 1080 $cm^{-1}$ corresponding to C-C-str vibration of MCH decreased rapidly and the band at 736 $cm^{-1}$ belonging to the ring breathing vibration mode of adenine appeared obviously. The result implies that there was no obvious change for the ssDNA SERS spectra when the substrates were treated with the concentration of MCH as low as 1 μM for 4h. In the following experiment, all substrates were treated by 10 nM MCH for 4h.

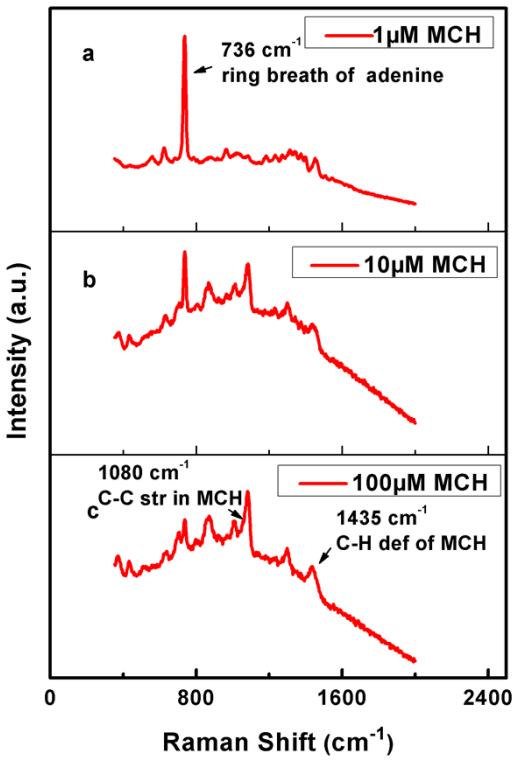


**Fig. S3**. SERS spectra of 10 μM adenine treated with different concentration of MCH （100 μM-1 μM).

**The reproducibility of the SERS measurements**

At first, the good spectral reproducibility was checked for the PCB77 binding aptamer without PCB77 binding. Seen from Fig S4, it demonstrates that the $SiO_2$@Au substrates can offer excellent reproducibility for SERS measurements of the aptamer

distributed on the surface of the $SiO_2$@Au core/shell NPs.

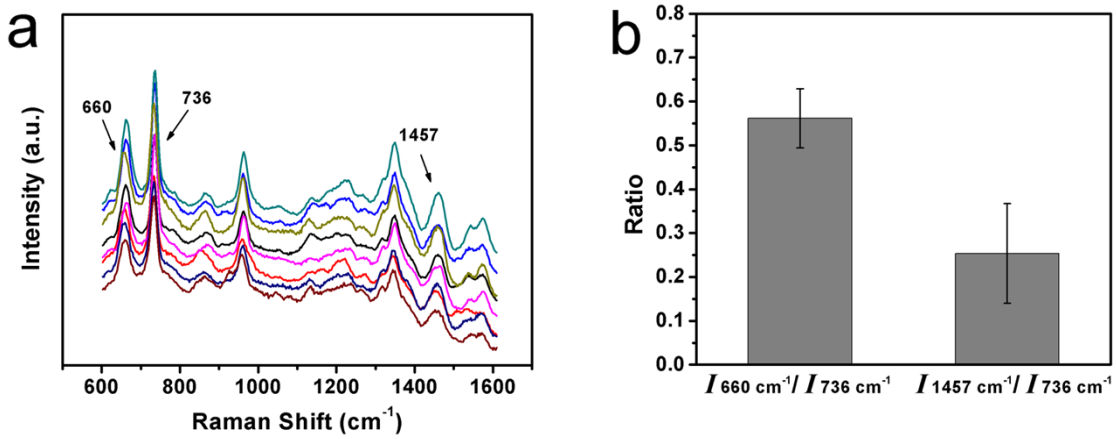


**Fig. S4**. **a:** The SERS average spectra of PCB77 binding aptamer on different eight substrates**. b:**The ratio of spectra bans of PCB77 binding aptamer in the same batch .

Secondly, the spectral reproducibility was checked via SERS mapping for the aptamer with the PCB77 binding. Fig. S5 shows the SERS spectra and imaging of the aptamer before and after addition of PCB77 in the same region. The results were consistent with the single point SERS measurements. The slight decrease of the SERS intensity of 736 $cm^{-1}$ may be attributed to the desorption of the aptamers on the Au surface when adding PCB77 to the substrate. The mapping result proves that the conformational changes of PCB77 binding aptamer were basically uniformed.

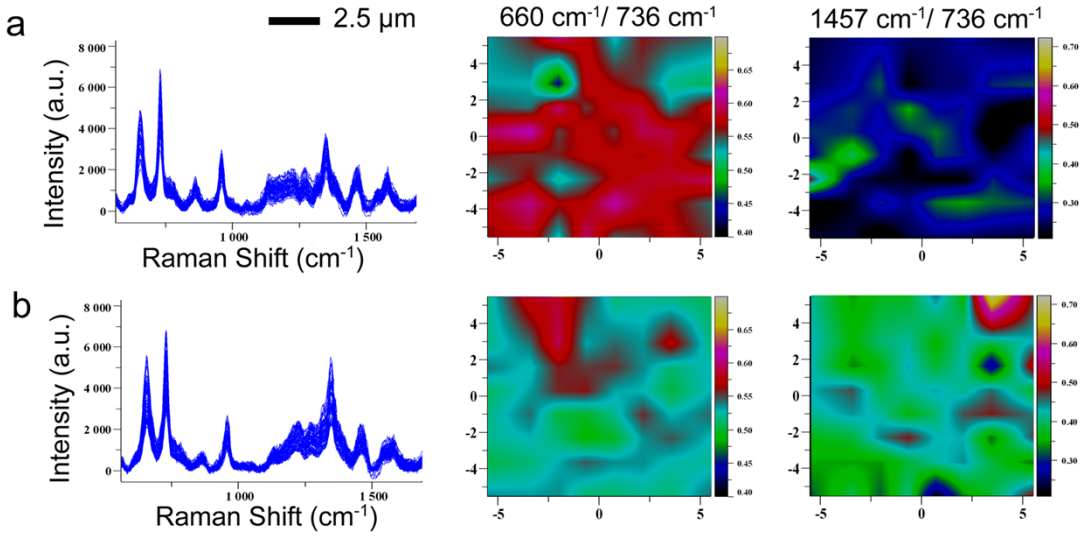


**Fig. S5**. SERS mapping of the PCB77 binding aptamer before (a) and after(b) addition of PCB77 ($1\times10^{-4}$ M) under the same condition.

**Specificity test for the PCB-77 binding aptamer**

In order to test the specificity of the PCB77-binding aptamer, the 20 μM PCB77 binding aptamer was conjugated on Au shell surface and was incubated with different concentrations of PCBs as shown in Fig. S6. The measurement and evaluation results can be seen in Fig. S7, and the Raman intensity ratios of I(1457 $cm^{-1}$)/I(736 $cm^{-1}$) were compared for PCB77 and other different types of PCBs. It confirms the good specificity for the as-fabricated SERS sensor.

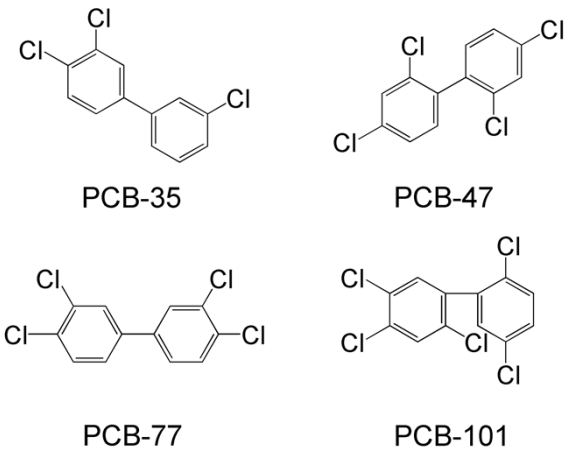


**Fig. S6. Chemical structures of PCBs used in this paper.**

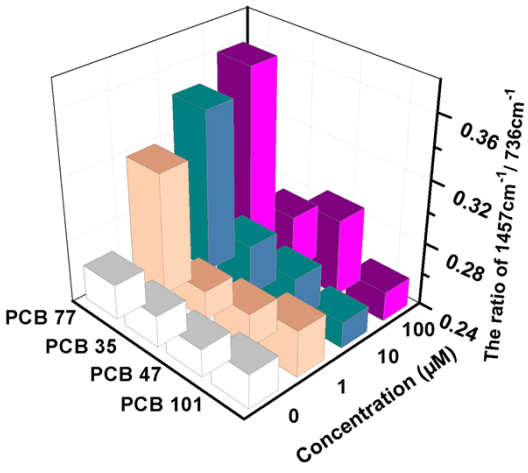


**Fig. S7. Specificity test for the PCB77-binding aptamer interacting with various PCBs at different concentrations.**

**Table S1. The Assignment of corresponding SERS bands**

| SERS frequency $cm^{-1}$ | Assignment | References |
|---|---|---|
| 660 | ring breath of G | 1 |
| 672 | C-S-C of DMSO | 2 |
| 736 | ring breath of A | 3 |
| 960 | $-NH_2$ Group on A | 4 |
| 1080 | C-C str in MCH | 5 |
| 1341 | str C5-N7, N-C2, bend C2-H, C8-H | 6 |
| 1435 | C-H def of MCH | 5 |
| 1457 | deoxyribose, adenine | 7 |

**Table S2. List of Abbreviation**

| **Abbreviation** | **Explanation** |
|---|---|
| TE buffer | 1 ×Tris EDTA buffer, pH=7.5 |
| piranha solution | $H_2SO_4$:$H_2O_2$=3:1 |
| NAP5 | purification columns (GE Healthcare) |
| TCEP | tris(2-carboxyethyl)phosphine |
| THPC | Tetrakishydroxymethylphosphonium chloride |
| MCH | mercaptoethanol |
| DMSO | dimethyl sulfoxide |
| APTMS | 3-aminopropyl)-trimethoxysilane |

**Table S3. Oligonucleotide Sequences used in the experiments**

| oligonucleotide | sequence |
|---|---|
| Oligomer I | 5’-SH-(CH2)6-GGCGGGGCTACGAAGTAGTGATTTTTTCCGATGGCCCGTG-3’ |
| Oligomer II | 5’-SH-(CH2)6-TTTTTTTTTTGGCGGGGCTACGAAGTAGTGATTTTTTCCGATGGCCCGTG-3’ |
| SH-A16 | 5'-SH-(CH2)6-AAAAAAAAAAAAAAAA-3' |

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