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Cysteamine-Modified Silver Nanoparticle Aggregates for Quantitative SERS Sensing of Pentachlorophenol with a Portable Raman Spectrometer

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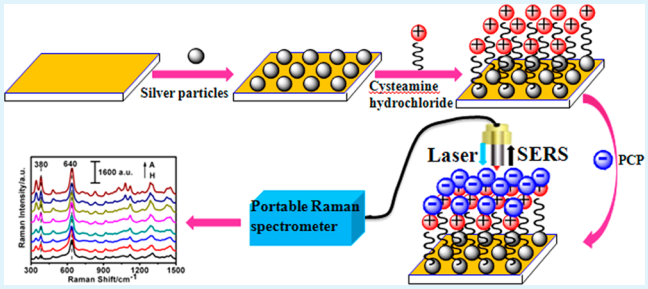
Supporting Information

ABSTRACT: Cysteamine-modified silver nanoparticle aggregates has been fabricated for pentachlorophenol (PCP) sensing by surface-enhanced Raman spectroscopy (SERS) using a portable Raman spectrometer. The cysteamine monolayers could preconcentrate PCP close to the substrate surface through the electrostatic interaction, which makes the SERS detection of PCP possible. Moreover, the Raman bands of cysteamine could be used as the internal spectral reference in the quantitative analysis. Qualitative detection of PCP was carried out by SERS without any sample pretreatment. Quantitative analysis of PCP was further realized based on the prepared substrate, as the log–log plot of normalized SERS intensity of PCP versus its concentrations exhibits a good linear relationship. The SERS signals collected on 20 randomly selected points show that the relative standard deviation of the normalized Raman intensity is 5.8%, which indicates the substrate had good uniformity. The PCP sensor also shows good long-term stability in the analyte solution. The substrate was cyclic immersed into PCP and methanol solution; after several cycles, the sensor still had good adsorption to PCP, which revealed the sensor has good reusability. Coupling with a portable Raman spectrometer, the cysteamine-modified silver nanoparticle aggregates have the potential to be used for in situ and routine SERS analysis of PCP in environmental samples.



KEYWORDS: *cysteamine, silver nanoparticle aggregates, quantitative, surface-enhanced Raman spectroscopy, pentachlorophenol*

INTRODUCTION

Pentachlorophenol (PCP), a common environmental contaminant, has been widely used as insecticide, herbicide, defoliant, disinfectant, and wood preservative.[1−3] PCP now can be detected in the air, water, soil, sediments, as well as in human urine, breast milk, blood, and adipose tissues.[1,4−6] Many studies indicate that PCP may cause the acute toxicities of organisms, endocrine disruptor and potentially carcinogenesis.[7−10] PCP has been classified as a priority pollutant by the U.S. EPA.[11] Therefore, it is of urgent need to develop simple, accurate, and sensitive analytical methods to measure PCP in the environment. Many assay methods have been established to realize the detection of PCP.[12] The traditional analytical methods include gas chromatography (GC) coupled with mass spectrometry or electron capture detectors (GC-MS or GC-ECD)[13−15] and high-performance liquid chromatography (HPLC) coupled with MS.[16] These methods indeed have good sensitivity, but they often involve complex and time-consuming sample pretreatment. There is still a necessity to develop a convenient, rapid, and sensitive method for field assays.

Surface-enhanced Raman spectroscopy (SERS), which can be used to conjunct with commercially available portable Raman systems, has been widely used in biology,[17] medicine,[18] or environmental monitoring[19−23] related fields. SERS has been considered to be a promising analytical technique for a variety of chemical- and biological-related molecules because of its good sensitivity, selectivity, fingerprint characteristics, and absence of interference from water.[24−26] However, there are still some limitations that restrict the technique as SERS is observed when the analytes are close to the rough noble metal surfaces.[27] Only these analytes with specific functional groups, like as thiol, carboxylic acid, amine, etc., could easily adsorb onto the substrate surface and provide good signals to meet the ultrasensitive analysis. Biological related samples often contain these functional groups and hence have good singnals.[28] However, a large group of organic pollutants in the environment characterized by nonfunctionalized groups, such as chlorinated pesticides, polycyclic aromatic hydrocarbons, trinitrotoluene, and other aromatic compounds, show weak affinity to gold or silver.[29] It is difficult to direct detect these compounds by SERS, and thus many indirect methods emerged.[22,30] Many methods rely on functionalized nano-

Received: December 11, 2012
Accepted: July 2, 2013
Published: July 2, 2013

particles with different media to concentrate analytes close to the substrate surface. These strategies include hydrophobic interactions using alkanethiols,[31,32] host−guest interactions using cyclodextrin,[33] specific interactions using antibodies[34] and aptamers,[35] as well as electrostatic attraction of ion pairing.[36] The surface modifier of the substrate may form a self-assembled monolayer (SAM) on the metal substrate, which could also be used as internal standards for the reliable quantitative assay.[30]

The work is aimed to provide a potential rapid, qualitative and quantitative application platform for monitoring of PCP contamination. In this paper, cysteamine hydrochloride (Cys)-modified silver nanoparticle aggregates were used for the detection of PCP based on SERS using a portable Raman spectrometer. Silver nanoparticle aggregates were used as the substrate because of its high SERS activity. Cys bears positively charged groups $-NH_3^+$, which could interact with the acidic PCP, hence, it was selected as the substrate modifier. Cys plays a dual role in the process: preconcentration of PCP close to the substrate surface through their electrostatic interaction and acting as the internal spectral reference in the quantitative detection. The integration times were just a few seconds and acceptable data could be obtained from the portable Raman spectrometer. Qualitative and quantitative SERS detection of PCP were carried out based on substrate. The uniformity, stability and reusability of Cys-modified substrate were evaluated. To the best of our knowledge, it is the first example to use Cys-functionalized substrate for SERS analysis of PCP.

EXPERIMENTAL SECTION

Chemicals. Silver nitrate, PVP-K30, sodium chloride (NaCl) and copper foils (Cu, 10 cm × 10 cm in size, 0.1 mm in thickness, 99.99%), and methanol were purchased from Sinopharm Chemical Reagent Co.,Ltd. Cysteamine hydrochloride (C_2H_7NS·HCl, 98%), pentachlorophenol (PCP, 1.01 mg/mL in methanol), tin dichloride ($SnCl_2·2H_2O$), and 1,4-dichlorobenzene (1,4-CB) were obtained from Aladdin Chemistry Co.,Ltd. 2-mercaptoethanol was obtained from Invitrogen. Citric acid-Na_2HPO_4 and Na_2CO_3−$NaHCO_3$ buffer solution were used in this work. P-chlorophenol (4-CP) was purchased from Shanghai Feixiang Chemical Co.,Ltd. (Shanghai, China). Ultrapure water (18.2 MΩ cm) was used throughout the experiment.

Preparation of Cys-Modified Ag/Cu Substrate. Silver nanoparticle aggregates on copper foil were used as the SERS-active substrate in this work, which has high SERS activity. The preparation of the substrate is based on the sequential redox cycles, in which the Ag^+ is reduced to elemental silver. By consecutive immersion of copper foil in the solutions of $SnCl_2$ and $AgNO_3$, silver nanoparticle aggregates were obtained on copper foil. The detailed preparation procedure for the substrate was described in our previous work.[37]

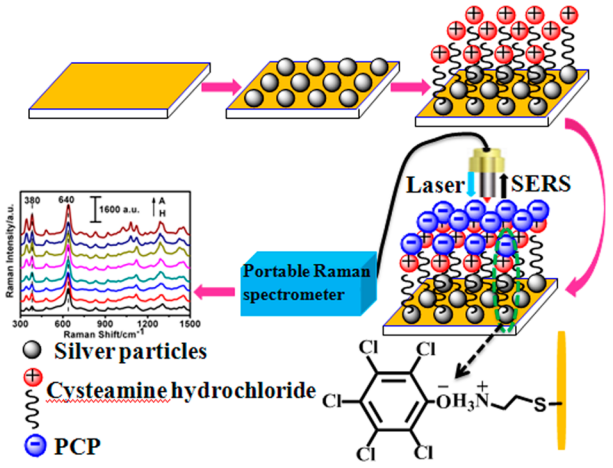
Modification of the substrate with Cys was performed in the ambient conditions, which has similar procedure with the previous literature.[38] The as-prepared substrate was immersed in the Cys solution in water for a certain time, rinsed with ultrapure water and allowed to air-dry. Cys-modified substrate was immersed in the analyte solution for 3 h and the Raman signals were collected then. The effects of salt concentration on detection were evaluated with addition of different concentration of NaCl in the PCP solution. The effect of pH on SERS detection was also evaluated. The analyte solution was prepared by diluting PCP stock solution in methanol to a desired concentration with ultrapure water.

Substrate Characterization and SERS Detection. The structure of the prepared substrate was characterized by X-ray diffraction (XRD) using a Bruker D8 advanced X-ray diffractometer equipped with graphite monochromatized Cu Kα radiation (λ = 1.5418 Å). The morphology of the prepared substrate was characterized by scanning electron microscope (SEM) (JSM-6700F). X-ray photoelectron spectroscopy (XPS) spectra were recorded by a PHI 5300 X-ray photoelectron spectrometer with Al Ka radiation. The pH values were measured with a Model pHS-3C digital pH meter (Shanghai, China). All the Raman measurements were performed with an Ocean Optics QE65000 spectrometer. The excitation wavelength was 785 nm, the input laser source of the instrument was operated at 440 mW and the maximun radiant power was 22 mW from the end of the probe (from the Users' Manual). The laser focus was about 158 μm, objective lens was about 7.5 mm, the actual power density was less than 1.1×10^6 W m^{-2}, and the integration time was 1 s for the SERS spectra unless the special note. All the spectra were baseline-corrected and calibrated with respect to the Raman mode of silicon at 520.7 cm^{-1}.

RESULTS AND DISCUSSION

Modification of the Substrate with Cys. Scheme 1 depicted the PCP sensing mechanism using SERS based on

Scheme 1. Schematic Representation of the Mechanism of Sensing PCP Using Cys-Modified Substrate as a SERS Sensor



Cys-modified silver nanoparticle aggregates as the substrate. The silver nanaoparticle aggregates on copper foil prepared via galvanic displacement reaction with $SnCl_2$ as the "sensitizer" were selected as the substrate, which was described in detail in our previous work.[37] The structure of the prepared silver nanaoparticle aggregates on copper foil was characterized by XRD and SEM. Figure S1A in the Supporting Information shows the XRD patterns of the prepared substrate, which revealed that the prepared substrate showed good crystallinity. Figure S2A in the Supporting Information shows the SEM image of the substrate, which confirms there are lots of silver nanoparticle aggregates on copper foil. Figure S3 in the Supporting Information shows the histogram of size distribution of the Ag nanoparticles on the substrate and the average size of Ag nanoparticle on the substrate is about 92.6 nm.

Modification of metal surface (Au or Ag) with thiols or disulfides has attracted considerable attention, as these substances could easily form well-organized SAM.[38] These SAMs have several important applications, such as modifying metal surface properties or immobilizing enzymes or electroactive molecules on electrodes. Cys has frequently been used as bifunctional building blocks, where the sulfur atoms binds to the metal surface while the amino groups could be used for the attachment of other molecules.[39−41] Cys monolayer has been used to immobilize DNA onto gold electrodes[42] or conjugate with Au nanoparticles for biobar-code assay.[43] In this work, the

dx.doi.org/10.1021/am401718p | ACS Appl. Mater. Interfaces 2013, 5, 6902−6908

Cys SAM was used for the adsorption of PCP. The formation of Cys monolayer on silver nanoparticles aggregates was studied by SERS and XPS. Figure 1 shows the Raman spectrum

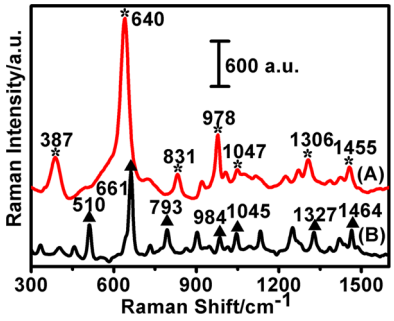


Figure 1. (A) SERS spectra of Cys on silver nanoparticle aggregates and (B) Raman spectrum of Cys powder.

of Cys powder and the SERS spectrum of Cys on the substrate. The characteristic SERS bands of Cys on the substrate appear at 387, 640, 831, 978, 1047, 1306, and 1455 cm^{-1}, which agreed well with the previous report.[44] We also recorded the Raman bands of Cys powder for comparison, as shown in Figure 1B. The SERS spectrum of Cys was comparable with the Raman spectrum of Cys powder, which indicated Cys had adsorbed on the substrate. XPS analysis was also conducted to testify the formation of Cys SAM on silver. Figure S4 in the Supporting Information shows the full XPS spectra of the substrate after it was immersed in the Cys solution. All the peaks in Figure S4 in the Supporting Information could be ascribed to Cu, Ag, S, C, or N elements. The inset of Figure S4 in the Supporting Information shows the enlarged view of the peak in the range of 156−168 eV, which centered at 162 eV. This peak is the S 2p spectrum, which could be attributed to a normal S−Ag bond. The XPS results further confirm that Cys had formed SAM on the substrate. The influence of concentration and immersion time on the formation of Cys SAM were also investigated. As shown in Figures S5 and S6 in the Supporting Information, the SERS intensity of Cys has little change with the variation of its concentration and immersion time. Ten mM Cys solution and 12 h immersion time were selected for use in this work. The XRD patterns and SEM image of the substrate after it was modified with Cys were shown in Figures S1B and S2B in the Supporting Informationand. It could be seen that Cys SAM has little influence on the structure and general morphology of the substrate.

Qualitative and Quantitative Detection of PCP Based on Cys-Modified Substrate. To confirm whether PCP could adsorb onto Cys-modified substrate, the substrate was immersed in 100 μM PCP solution for 3 h and their SERS spectra were recorded. The SERS spectrum of PCP on Cys-modified substrate is illustrated in Figure 2A. The Raman spectrum of PCP was also shown for comparison as shown in Figure 2B, which agrees well with the previous reports about the FT-Raman spectrum of the powder sample of PCP.[45] After immersed Cys-modified substrate into PCP solution for 3 h, new Raman bands at 340 cm^{-1} (C−O bending and ring deformation), 380 cm^{-1} (out of plane ring deformation), 481 cm^{-1} (C−O stretching), 1120 and 1535 cm^{-1} (ring stretching) labeled with symbols appeared on the spectrum,[23,45,46] which are the characteristic peaks of PCP. Hence, it could be confirmed that the detection of PCP could be realized based on

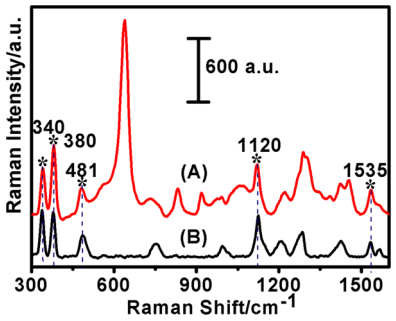


Figure 2. (A) SERS spectrum of PCP on Cys-modified substrate and (B) Raman spectrum of PCP for comparison.

Cys-modified substrate. To examine the influence of immersion time on the detection, we investigated the kinetic curve about PCP adsorption. Cys-modified substrate was immersed into PCP solution for different time from 6 min to 3 h. Figure S7 in the Supporting Information shows the kinetics of PCP adsorption. It could be seen that the adsorption reached saturation within 6 min for the solution with 10 μM initial PCP concentration. For the solution with 1 and 0.5 μM initial PCP concentration, the saturated adsorption time was 68 and 113 min, respectively. To ensure all the test solution has reached adsorption equilibrium, a relative long time of 3 h was selected for PCP adsorption to get reliable SERS results.[20]

To confirm whether Cys plays a major role in the adsorption of PCP, we have performed a control experiment involving unmodified SERS substrate exposed to PCP. Weak PCP signals could be detected without the Cys monolayer on the substrate, as shown in Figure S8B in the Supporting Information, which further illustrates that the Cys monolayer plays a major role in adsorbing PCP close to the substrate surface, where the $-NH_3^+$ groups of Cys acted as the receptor to bind PCP through the electrostatic interaction.[44,47−49] 2-Mercaptoethanol was also selected as the substrate modifier to detect PCP. The SERS data of PCP on the 2-mercaptoethanol modified substrate was shown in Figure S9 in the Supporting Information. Compared the SERS data of PCP on 2-mercaptoethanol-modified substrate with that on Cys-modified substrate, it could be seen that only weak PCP signals were detected on the 2-mercaptoethanol modified substrate. This is ascribed to the protonated $-NH_3^+$ groups of Cys has stronger affinity to PCP than the −OH group of 2-mercaptoethanol.[47−49] This control experiment further confirms it is a good choice to select Cys as the modifier to detect PCP.

The effect of salt concentration on detection of PCP was evaluated. The initial PCP concentration was 10 μM and the initial NaCl concentration was varied from 0 to 10000 μM. Figure S10 in the Supporting Information shows the histogram of the normalized Raman peak intensity at 380 cm^{-1} of PCP with the increasing of NaCl concentration. As shown in Figure S10 in the Supporting Information, the SERS intensity of PCP decreased with the increase of salt concentration. Once the concentration of the added salt was more than 500 μM, the SERS signals of PCP decreased markedly. This result implies that increase in ion strength would interference the interaction of PCP and the substrate.[50]

The required pH condition for such electrostatic interaction between cysteamine and PCP has been evaluated. The PCP solutions were adjusted to pH 3.0−11.0 with citric acid-Na_2HPO_4 and Na_2CO_3−$NaHCO_3$ buffer solution. Figure S11 in the Supporting Information shows the normalized Raman

peak intensity at 380 cm^{-1} of 10 μM PCP as the function of pH values. It is noted that the Raman intensity increased as the pH value varied from 4.0 to 5.0 and leveled off from pH 10.0 to 11.0. When the pH value is higher than 10, Cys is deprotonated,[51−53] which would decrease the affinity of the substrate to PCP. The Raman intensity of PCP was not significantly affected by the solution pH value over the pH range of 5.0−10.0. All the experiments were performed at pH value between 5.0 and 10.0.

To evaluate the sensor sensitivity to PCP, the substrates were immersed into PCP solution with various concentrations ranging from 100 to 0.5 μM, and their corresponding SERS spectra were recorded. Figure 3 shows the SERS spectra of PCP

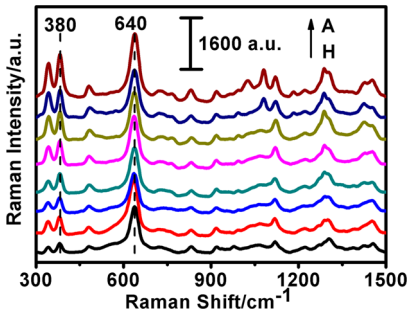


Figure 3. SERS spectra of PCP on Cys-modified substrate with concentrations of (A) 100, (B) 50, (C) 25, (D) 10, (E) 5, (F) 2.5, (G) 1, and (H) 0.5 μM.

with increasing concentrations based on Cys-modified substrate. The characteristic Raman bands of PCP were quite sensitive to its concentrations and increase gradually with the increasing of the analyte concentration. Quantitative SERS analysis of PCP was also carried out. The characteristic peak at 380 cm^{-1} was selected as the function of the PCP concentration. As the concentration of Cys was a fixed value in this quantitative experimental process, the intensity of its Raman bands could be considered as constant. The calibration curve for PCP was plotted based on the internal reference method, which could provide a reliable way to investigate the correlation between molecular structures and their SERS activities.[54] The curve was constructed using the normalized Raman bands intensity of PCP at 380 cm^{-1} and the most obvious Raman band of Cys at 640 cm^{-1} was used as the reference. As seen in Figure 4A, the normalized Raman signal intensity of PCP increases with the increasing concentrations of the analyte. The log−log plot of the normalized Raman intensity of PCP at 380 cm^{-1} versus its concentration exhibits a good linear correlation, as shown in Figure 4B. The linear regression equation is $y = -0.55 + 0.15x$ (where x is logarithm of the PCP concentration and y is logarithm of the normalized SERS intensity of Raman peak at 380 cm^{-1}) with the correlation coefficient of 0.97. The detection limit of PCP was 0.20 μM (3 times the standard deviation above the blank). The proposed method has a comparable or superior linear range and detection limit compared with other methods for PCP detection, which are summarized in Table S1 in the Supporting Information. The SERS detection of PCP using Cys-modified substrate has similar quantitative results (a good linear relationship of the log−log plot) as SERS detection of PAHs using alkanethiols modified substrate.[37,55] The adsorption between the substrate and the analyte solution at equilibrium could use adsorption isotherm equations[56] to describe. It is assumed that n molecules of PCP interact with Cys on the substrate surface, the following equilibrium could be considered as reasonable

$$[\mathrm{Cys}] + n[\mathrm{PCP}] \rightleftharpoons [\mathrm{Cys{\cdot}PCP}_n] \quad (1)$$

The equilibrium constant (K) could be written as

$$K = \frac{[\mathrm{Cys{\cdot}PCP}_n]}{[\mathrm{Cys}][\mathrm{PCP}]^n} \quad (2)$$

then

$$\log([\mathrm{Cys{\cdot}PCP}_n]/[\mathrm{Cys}]) = \log K + n\log[\mathrm{PCP}] \quad (3)$$

where [Cys] is the concentration of Cys adsorbed on the substrate surface, [PCP] and [Cys·PCP_n]are the concentrations of PCP in the liquid matrix and on the Cys-modified substrate. As the used volumes of PCP solutions were relative large in our detection system, [PCP] is approximately equal to c_0 under equilibrium conditions, where c_0 is the initial concentration of PCP in the liquid matrix.

The eq 3 could be deduced to the following format

$$\log([\mathrm{Cys{\cdot}PCP}_n]/[\mathrm{Cys}]) = \log K + n\log c_0 \quad (4)$$

as

$$I_{\mathrm{SERS}} \propto NI_{\mathrm{L}}|A(\nu_{\mathrm{L}})|^2|A(\nu_{\mathrm{S}})|^2\sigma^{\mathrm{R}}_{\mathrm{ads}} \quad (5)$$

[57] where I_{SERS} is the SERS signal, N represents the molecular number involved in the SERS process, I_L represents the excitation intensity, and $A(\nu_L)$ and $A(\nu_S)$ are excitation and scattered field enhancement factors, respectively. σ^R_{ads} is the increased Raman cross-section of the adsorbed molecule compared to that in a "normal" Raman experiment σ^R. I_{SERS} depends on I_L and an effective SERS cross-section (σ^{SERS}_{eff} =

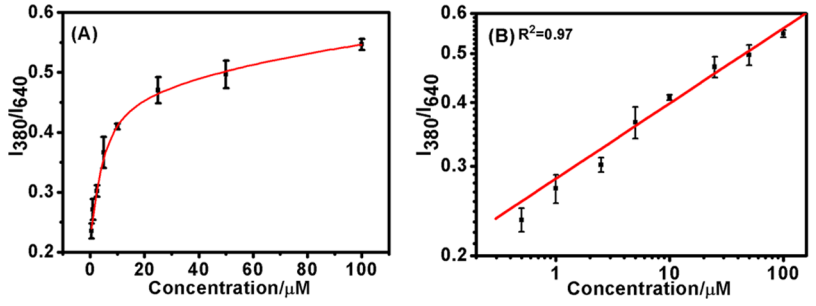


Figure 4. (A) Calibration curve and (B) log−log plot for PCP based on Cys-modified substrate. The data points correspond to the average ± standard deviation of five measurements.

$\sigma^{R}_{ads}A(\nu_L)^2A(\nu_S)^2$). σ^{SERS}_{eff} benefits from the EM effect (described by $A(\nu_L)$ and $A(\nu_S)$) and chemical enhancement effect (expressed by the σ^{R}_{ads}). In an established experimental process, I_L and σ^{SERS}_{eff} could be considered as constant. Hence, the written $I_{SERS} = aN$ could be considered as reasonable, where a is a constant, which is not related to N and includes all other related parameters. It is assumed that only these PCP molecules adsorbed on the substrate surface by Cys make contributions to the SERS intensity ($I_{SERS,\ PCP}$). Thus, $N = b$[Cys·PCP], $I_{SERS,\ PCP} = c$[Cys·PCP], and $I_{SERS,\ Cys} = d$[Cys], where c (d) is a constant that is not related to PCP (Cys) concentration and includes all Raman and SERS related parameters. The eq 4 could be deduced to the following format

$$\log(I_{SERS,PCP}/I_{SERS,Cys}) = \log K' + n\log c_0 \quad (6)$$

As a, b, c, and d are constant, K' is also constant. From eq 6, it could be interpreted that the good linear relationship of the log−log plot is reasonable.

To evaluate the practical application of the developed method, the Cys-modified silver nanoparticle aggregates was applied to determine PCP in tap water and spring water samples. The results of recovery for real water samples of the proposed method were obtained and compared with those of HPLC. The analytical performances are summarized in Table S2 in the Supporting Information.

These results indicate that Cys-modified silver nanoparticle aggregates could realize quantitative or semiquantitative analysis of PCP in aqueous media. The technique in conjunction with readily available and relatively inexpensive portable Raman spectrometers has the potential to be used as a rapid analytical tool for environmental pollutants.

Uniformity, Stability, and Reproducibility of Cys-Modified Substrate. It is well-known that the uniformity and stability of the substrate are important parameters for SERS detection. It has been reported that uniformity of the substrate is one of essential parameters for generating quantitative SERS data.[58] Nonuniformity of the substrate often leads to poor reproducibility of the SERS signals. The uniformity of Cys-modified substrate was evaluated in this work. To illustrate the uniformity of the substrate, the SERS spectra were recorded on 20 randomly selected points of one substrate. Figure 5 shows the SERS spectra from 20 randomly selected points on one substrate, which were normalized using the Raman peak of Cys at 640 cm^{-1} as a reference. The inset image of Figure 5 represents the normalized intensity change of PCP Raman bands centered at 380 cm^{-1}, and the relative standard deviation of the normalized intensity is 5.8% from these different points, which indicated that Cys-modified substrate has excellent uniformity across the entire area. Furthermore, the stability of Cys-modified substrate in an aqueous solution was also investigated. Figure 6 shows the SERS spectra of PCP on the freshly prepared substrate and the substrate immersed in its solution for 5 days. It could be seen that neither the PCP spectrum band positions nor the Raman bands intensity had obvious change after immersed in the PCP solution for 5 days, revealing that the Cys-modified substrate could be stable at least for a 5-day period in an aqueous solution. This long-term stability of the substrate in the analyte solution is of great importance for real-time environmental pollution monitoring in practical application.

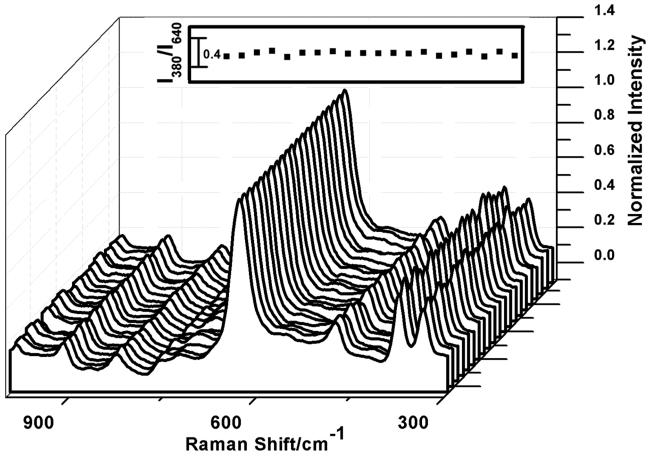


Figure 5. The uniformity of Cys-modified substrate probed with 10 μM PCP, the SERS spectra were normalized using the Raman peak of Cys at 640 cm^{-1} as the reference. Inset shows the changes of the Raman band of PCP centered at 380 cm^{-1}.

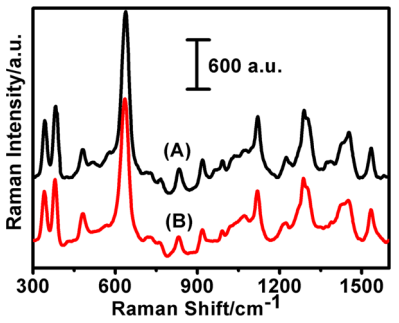


Figure 6. Long-term stability of Cys-modified substrate. SERS spectra of 10 μM PCP obtained from (A) the freshly prepared substrate and (B) the substrate immersed in the analyte solution for 5 days.

Other than the uniformity and stability, an ideal SERS sensor would also facilitate reversible partition of the analyte so that substrate is reusable.[20] In this work, the reusability of the Cys-modified substrate was evaluated through examining the partition/departition process of PCP. Cys-modified substrate was cyclic immersed in the solution of PCP and methyl alcohol, then their corresponding SERS spectra were recorded (Figure 7). The appearance of the new Raman bands centered at 340, 380, 481, and 1120 cm^{-1}, which are ascribed to the characteristic Raman peaks of PCP, represents the analyte had partitioned into the Cys monolayer after the substrate was immersed in the PCP solution for 1 h. As shown in Figure 7B, D, F, and H, after the substrate was immersed into methyl alcohol for 1 min, the characteristic Raman peaks of PCP disappeared, which indicated that PCP had been eluted from the Cys monolayer. Comparing Figure 7H with 7A, it could be seen that the two spectra are still quite similar, which indicated that the Cys-modified substrate still had good adsorption effect to PCP after four cycles. The above results illustrated the substrate had good reusability. Hence, using Cys-modified substrate for SERS detection of PCP is reasonable.

Selectivity of the Cys-Modified Substrate to PCP. In order to evaluate the selectivity of the Cys-modified substrate to PCP, the substrate was applied in SERS sensing of the complex mixtures of PCP and its analogues (their structures are shown in Figure S12 in the Supporting Information). The SERS spectra were measured as shown in Figure 8. According to the experiments, at 100 μM concentration in methanol, only

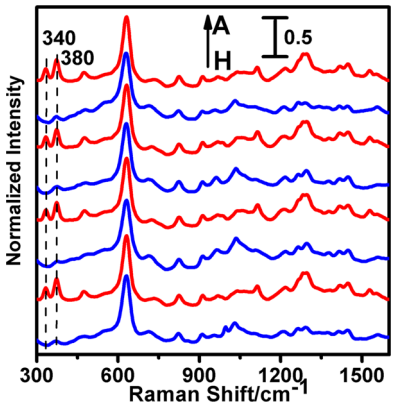


Figure 7. Reusability of Cys-modified substrate. (A, C, E, G) The substrate was immersed in 100 μM PCP for 1 h. (B, D, F, H) The substrate was immersed in methyl alcohol for 1 min. All the SERS spectra were normalized using the Raman peak of Cys at 640 cm^{-1} as the reference.

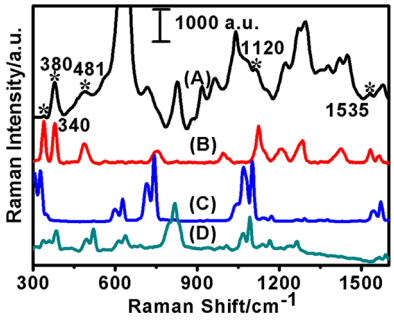


Figure 8. (A) SERS spectrum of the substrate immersed in mixture of PCP, 1,4-CB, and 4-CP. The normal Raman spectrum of (B) PCP, (C) 1,4-CB, and (D) 4-CP for comparison.

the Raman peaks of PCP appeared in Figure 8A, other analytes such as 1,4-dichlorobenzene (1,4-CB) and p-chlorophenol (4-CP) were not detected on the substrate. These results showed that the examined coexisting organic compounds hardly interfered with the PCP determination.

CONCLUSIONS

This work developed a rapid qualitative and quantitative SERS sensor for PCP. Cys-modified silver nanoparticle aggregates were used as the substrate for SERS detection of PCP using a portable Raman spectrometer. Acceptable data could be obtained within just a few seconds from the portable Raman spectrometer in our work. Qualitative SERS detection of PCP was realized, as Cys could adsorb PCP close to the substrate surface through electrostatic interaction. Quantitative SERS detection of PCP was also realized as the log–log plot of the normalized Raman intensity of PCP to its concentration exhibits a good linear relationship. This method achieved quantitative detection of PCP ranging from 0.5 to 100 μM and provided a detection limit of 0.2 μM. Cys monolayer plays a dual role in the SERS process: adsorption of PCP close to the substrate surface and acting as the internal reference in the quantitative analysis. Cys-modified substrate shows good uniformity, long-term stability and reusability. These results show Cys-modified silver nanoparticle aggregates could be used as a good substrate for routine SERS analysis of environmental pollutants.

ASSOCIATED CONTENT

Supporting Information

XRD patterns, SEM images and XPS spectra of the substrate, SERS spectra of the substrate after immersed in Cys with different concentrations for different time, kinetics of PCP adsorption, SERS spectra of PCP on unmodified and 2-mercaptoethanol modified substrate, effect of salt concentration and solution pH on the detection of PCP. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We are grateful for financial support from National Basic Research Program of China (973 Program 2013CB934301), National Natural Science Foundation of China (NSFC21075077 50972083 and 91023011), Shandong Provincial Natural Science Foundation for Distinguished Young Scholar (2010JQE27013), Independent Innovation Foundation of Shandong University (IIFSDU- 2012JC027).

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