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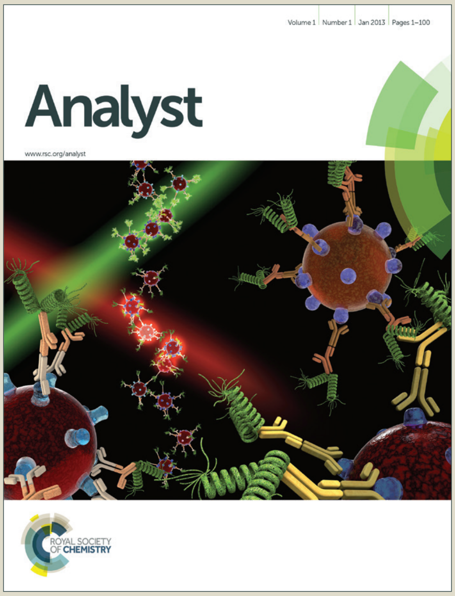

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ARTICLE

Sliver nanoplates decorated copper wire for on-site microextraction and detection of perchlorate using portable Raman spectrometer

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Perchlorate, causing health effect on thyroid function, is highly soluble and movable in the environment. In this work, diethyldithiocarbamate (DDTC) modified sliver nanoplates were fabricated on the copper wire to perform the on-site microextraction and detection of perchlorate. This fiber could be inserted into water or soil to extract perchlotare through electrostatic interaction and then detected by a portable Raman spectrometer owing to its surface enhanced Raman (SERS) activity. A relative stable vibrational mode (δ(HCH)(CH_3), (CH_2)) of DDTC at 1273cm^{-1} was used as an internal standard, which was little influenced by the absorption of ClO_4^-. The DDTC modified Ag/Cu fiber showed high uniformity, good reusability and temporal stability under continuous laser radiation with the RSD lower than 10 %. Qualitative and quantitative detection of perchlorate were also realized. A log-log plot of the normalized SERS intensity against perchlorate concentration showed a good linear relationship. The fiber could be also directly inserted into the perchlorate polluted soil and the perchlorate could be on-site detected. The detection limit in soil reached 0.081 ppm, which was much lower than the EPA published safety standard. The recovery of the detection was 105 % and comparable with the ion chromatography. This hyphenated method of microextraction with direct SERS detection may find potential application for direct pollutants detection free from complex sample pretreatment.

Introduction

Perchlorate is both naturally and manmade that has been widely used as solid rocket propellant and explosives ingredient.[1, 2] Perchlorate could be also present in soil, fertilizers and bleach.[3] It has caused wide public concern over the recent years because it probably has health effect on thyroid function through inhibiting the iodide uptake.[5, 6] Due to its high solubility and movability, perchlorate usually migrates quickly from soil to ground water, crops, vegetables, fruits and other existing forms.[7-10] Perchlorate in soil might be also accumulated by plants or wildlife exposed to human beings.[4] It is a chanllenge before us to find a convenient, sensitive and selective method to on-site preconcentrate and detect perchlorate in soil.[11, 13, 14] The general detection methods of perchlorate performed in laboratory are ion chromatography (IC),[15-17, 23] electrospray ionization (EI)[18, 19] liquid chromatography (LC)[20, 21] and mass spectrometry (MS).[22, 24]

Efficient sample preparation techniques, aiming to let the analytes separate from the complex sample matrix, are desired before detection.[12] Liquid–liquid extraction (LLE)， Solid-phase extraction (SPE), Solid-phase microextraction (SPME) are generally applied to gaseous, aqueous and solid samples matrix.[25] SPME is a simple, solvent-free on-site sampling method to separate and preconcentrate target compounds of low concentration from various sample matrices.[26, 27] The conductive polypyrrole (PPY) film was coated on a platinum wire to extract perchlorate from aqueous solutions.[44] Then the PPY films were transferred to NaCl solution to release the analyte based on ion exchange. A positive or negative potential was usually needed during this process. The released sample analyte solution was detected by the HPLC coupled with ionization electrospray MS.

Surface enhanced Raman spectroscopy (SERS), due to its fine sensitivity, selectivity and fingerprint characteristics, has been widely used in the analysis of chemical and biological samples.[31, 32] The enhancement effect of SERS generally derives from electromagnetic and chemical factor. The electromagnetic effect is dominant while the chemical effect contributes only one or two order of magnitude.[35] Chemical enhancement results from charge-transfer between adsorbate and metallic (Ag or Au) surface. The electromagnetic enhancement effect usually depends on the shape and size of the metallic nanostructures.[46] Ag nanoparticles were usually fabricated with SERS enhancement of 10^6, while the enhancement factor of Ag nanoplates with anisotropic structures sometimes could reach 10^9 owing to their broad localized surface plasmon resonance in the near infrared spectrum.[29, 30, 38, 40] Sliver nanoplates or other nanostructures were usually fabricated in colloids or solid substrates.[45] Moreover, sliver nanoparticles could be also decorated on the filter membrane as a flow-through SERS substrate which avoided the repeated preparation and separation process.[36]

In this article, the DDTC modified Ag nanoplates were fabricated on a copper fiber combining the advantages of SPME and SERS. The sliver nanoplates were fabricated on the fiber on account of its high SERS activity. Diethyldithiocarbamate (DDTC) was selected to modify the sliver nanoplates due to its adsorbability to perchlorate. This fiber could be directly inserted into solution or soil sample to extract perchlorate and detected with a portable Raman spectrometer. This hyphenated method avoided the sophisticated sample pretreatment, providing an on-site detection approach.

Experiment

Chemicals

Silver nitrate (AgNO$_3$), 2-nitrobenzoic acid, sodium diethyldithiocarbamate (DDTC), copper wire (Cu, 0.6 mm in diameter, 99.99%), ethanol and acetone were purchased from Sinopharm Chemical Reagent Co.Ltd. (shanghai,China). Sodium perchlorate (NaClO$_4$.H$_2$O) was purchased from Aladdin Chemicals. Perchlorate was dissolved in ultrapure water (with a resistivity of 18.2 MΩ·cm^{-1}) to obtain 10^{-2} M solution for further use.

Characterization techniques

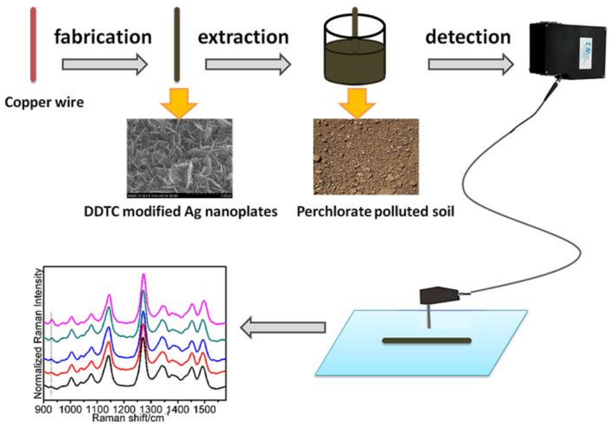
A Bruker D8 advanced X-ray powder diffractometer with graphite monochromatized Cu Kα radiation (λ=0.15418) was for obtaining the X-ray diffraction (XRD) patterns of the structure of the Ag/Cu fibers. An S-4800 Scanning Electron Microscopy (SEM) with the 15.0 KV accelerating voltage was used to characterize the morphology of the Ag/Cu fibers. An Oxford INCA sight X Energy-dispersive X-ray spectroscopy (EDS) and A ThermoFisher SCIENTIFIC ESCALAB 250 X-ray photoelectron spectroscopy (XPS) spectra were taken to certify if the Ag/Cu fiber was modified by DDTC successfully. An Ocean Optics QE65000 Raman spectrometer equipped with a TE cooled FFT-CCD detector was operated throughout to measure the SERS signal on the DDTC modified Ag/Cu fiber. The excitation wavelength was 785 nm and the operated input laser source was 440 mW and the maximum power was 455 mW. The diameter of the laser focus and the objective were about 158 μm and 7.5 mm， respectively. All the accumulation time of the SERS measurement was 1s. All the spectra were calibrated with standard silicon wafers with reference to the Raman mode of silicon at 520.7 cm^{-1}. A Model pHS-3C digital pH meter (Shanghai, China) was served to measure the pH values. An ion chromatography of ICS-900 was used to detect perchlorate in soil for comparision.

Fabrication of DDTC-modified Ag/Cu fiber

Copper wires (1 cm) were rinsed with acetone, ethanol and ultrapure water in ultrasonic cleaner for 10 min in turn. The silver nanoplates on the fiber were prepared by galvanic displacement reaction according to our previously published methods.[38] In brief, the copper fiber was dipped into a solution of silver nitrate (10 mM) and 2-nitrobenzoic acid (10 mM). The color of the copper fiber turned into black grey rapidly and the reaction proceed for 5 min at ambient temperature in order to form uniform Ag nanoplates. Then the short fiber was taken out and rinsed with ultrapure water. After that, the fibers were immersed into a well prepared DDTC solution (10 mM) for 30 min. The fiber turned dark brown due to the modification of DDTC. After the modification, the DDTC modified Ag/Cu fiber was taken out and rinsed with ethanol and ultrapure water.

The extraction and fiber analysis

On account of the non-volatile character, the perchlorate was preconcentrated by direct immersion solid phase microextraction method. In water sample, the DDTC modified Ag/Cu fiber was directly immersed into the solution for 6 h at ambient temperature. It seemed that electrostatic interaction contribute to the retention of the perchlorate on the DDTC modified Ag/Cu fiber.[28] Amino groups on the fiber are thought to interact with ClO$_4^-$. The extraction in soil was also performed using direct immersion method in a water-soil (slurry) mixture.[57-59] Fibers removed from slurries rinsed completely of residual soil with ultrapure water. After the perchlorate was



Scheme 1. Schematic representation of the process of microextraction and determination of perchlorate using DDTC modified Ag/Cu fiber.

extracted by the DDTC modified Ag/Cu fiber, the fiber was pulled out for SERS detection with 455 mW laser power and 1s acquisition time. The fiber was laid on a tinfoil covered glass sheet and scanned with laser starting at 1.0 mm from the fiber tip with an interval of the detection spots around 1.0 mm. The focus was adjusted to different positions surrounded the fiber to make the detection more omnidirectional.

Moreover, the extraction conditions of perchlorate were evaluated. The influence of pH value for Raman detection was estimated. The interference of co-existing ion on the extraction of perchlorate was investigated by adding salts in perchlorate solution, including NaCl, KNO_3 and Na_2SO_4. The extraction time was also evaluated by measuring kinetic curves of perchlorate with different concentrations.

Results and discussion

Characterization and evaluation of the DDTC modified Ag/Cu fiber

Scheme 1 described the perchlorate detection process by SERS based on the DDTC modified Ag/Cu fiber. The Ag/Cu fiber was fabricated by the modified galvanic displacement reported in our previous work. The 2-nitrobenzoic acid was used to adjust the morphology of the silver nanocrystals. And 2-nitrobenzoic acid was easy to adsorb on the Ag (111) which led to the formation of Ag nanoplates.[38] The XRD patterns and SEM image of the Ag/Cu fiber (Figure S1and Figure S2) characterized its structure and morphology. The XRD patterns showed that the Ag/Cu fiber had good crystallinity. The SEM image revealed that the surface of copper wire was covered by homogeneous silver nanoplates from galvanic displacement reaction.

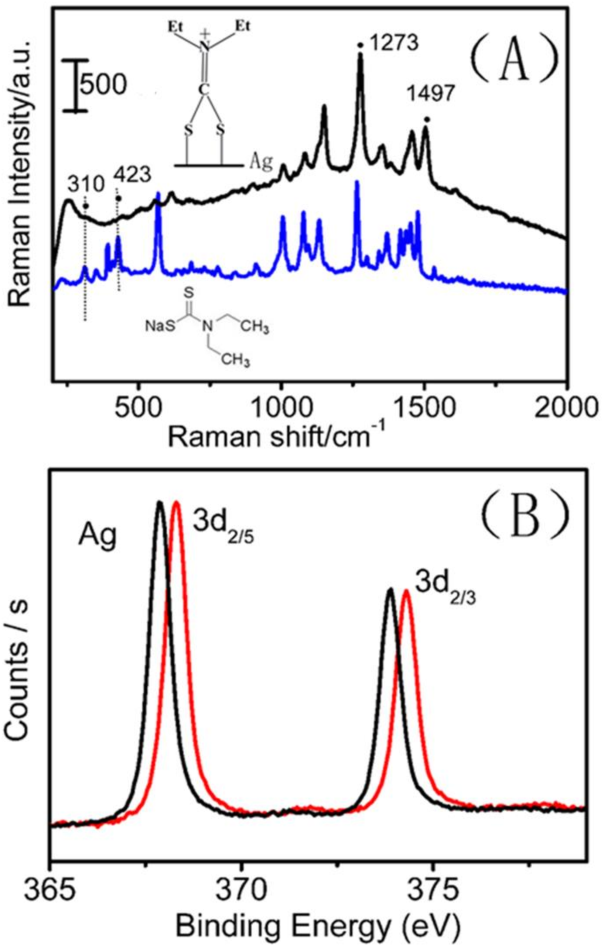


Figure 1. (A) SERS spectra of DDTC modified Ag/Cu fiber (black) and Raman spectrum of DDTC powder (blue). (B) XPS spectra of the Ag (3d) scan of the Ag/Cu fiber before (red) and after (black) modified with DDTC.

DDTC was used as an extraction adsorbent to preconcentrate the perchlorate taking advantage of the electrostatic reaction between DDTC and perchlorate. As showed in Figure S3, DDTC modified Ag/Cu fiber containing the $^+N(CH_2CH_3)_2$ group could absorb the electronegative perchlorate (ClO_4^-). Figure 1 represented the characterization of the DDTC modified Ag/Cu fiber. From Figure 1A we could see that the DDTC was successfully modified on the Ag/Cu fiber. The characteristic Raman bands of DDTC on the Ag/Cu fiber appear at 1273 cm^{-1}, 1079 cm^{-1}, 1343cm^{-1} and 1453cm^{-1}, 1497 cm^{-1} which agreed exactly with the previous report. The SERS spectra peak at 1497cm^{-1} was assigned to the $\nu_{as}(C{=}N)$ $+\delta(HCH)(CH_2)$ sciss.[47] The Raman peaks of DDTC powder at 310 cm^{-1} and 423 cm^{-1} were respectively assigned to the N-C=S in plane bending and the S=C-S strech,[54] while these two peaks almost disappeared in the SERS spectrum recorded on the DDTC modified Ag/Cu fiber. They both indicated that the primary adsorption manner of DDTC was bidentate configuration. This modification process led to the redistribution of the free electron pair in N atom and the formation of the C=N$^+$ bonding.[55] The XPS spectra confirmed the modification process. Figure 1 B showed the binding energy of Ag (3d) for the Ag/Cu fiber before and after DDTC modification. The fact that the binding energy of Ag ($3d_{5/2}$) shifted to lower value by 0.45 eV and the Ag ($3d_{3/2}$) shifted to lower value by 0.42 eV might be caused by the interaction of DDTC and silver nanoplates and the formation of the Ag-S binding. [51, 53] In addition, The XPS represented the binding energy of S (2p) at 162 eV after modification, which was consistent with previous literature.[37](Figure S4A).The EDS spectra further verified the modification process. The peaks on EDS spectra for Ag, Cu and S element indicated the DDTC was linked to the surface of the Ag/Cu fiber (Figure S4B).

The effects of different concentrations and immersion time of DDTC modification were also evaluated. The Ag/Cu fibers were immersed into 5 ml different concentrations of DDTC solutions for 30 min to investigate the modification concentration while the immersion time was investigated by immersing the fiber in a 10 mM DDTC solution for different time.(SI 5 and 6). Figure S5 and S6 confirmed that the SERS intensity scarcely changed with the variation of its concentration and immersion time when the adsorption of DDTC has reached saturation.[39] Eventually, 10 mM DDTC solution and 30 min immersion time were selected to modify the Ag/Cu fiber.

Figure S7B showed that the Raman peaks of the sodium perchlorate (dehydrated) was about at 951cm^{-1} assigned to the symmetric stretch for ClO_4^-.[33] The SERS spectrum of the DDTC modified Ag/Cu fiber (Figure S7A) showed that there were no signal interference in the spectral region between 900 and 980 cm^{-1}. Thus, using these DDTC modified Ag/Cu fibers for the detection of perchlorate was possible.

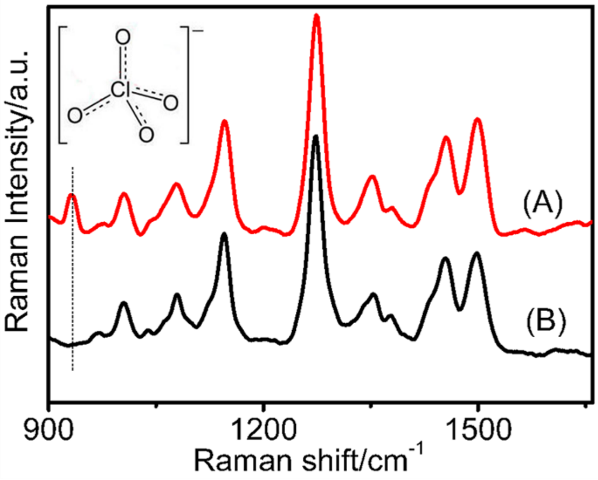


Figure 2. (A) SERS spectrum of perchlorate of 10 μM extracted on the DDTC modified Ag/Cu fiber. (B) SERS spectrum of DDTC modified Ag/Cu fiber for comparison.

Qualitative detection of perchlorate on the DDTC-modified Ag/Cu fiber

In order to confirm whether the perchlorate could be extracted onto the DDTC modified Ag/Cu fiber, the fiber was immersed in a 10 μM perchlorate solution for 1 h and the SERS spectrum was recorded (Figure 2). The characteristic Raman peak of perchlorate at 932 cm^{-1} (Figure S8) showed a left shift compared to the Raman peak of perchlorate powder at 951 cm^{-1}, which was attributed to the interaction or sorption of ClO_4^- with Ag nanoplates.[48] After the Ag/Cu fiber was modified with DDTC, perchlorate could be detected while there was no perchlorate signal on the bare Ag/Cu fiber (Figure S9), indicating that it was necessary to use the DDTC modifier to extract perchlorate.

Stability, Uniformity and Reproducibility

The stability, uniformity and reproducibility are important parameters for credible quantitative SERS detection.[31] The temporal stability of the fiber was evaluated by obtaining continuous SERS spectra under continuous laser radiation as shown in Figure 3A. These SERS signals were acquired within 120 s with an interval time of 2 s. The RSD of the Raman peak height signal at 932cm^{-1} was 0.64 %. The stability of this fiber might be derived from electron redistribution between copper and silver nanoplates which protected silver nanoplates from oxidizing.[38]

To evaluate the uniformity of fiber, The SERS spectra of 20 points, randomly selected from a DDTC modified Ag/Cu fiber probed with 10 μM perchlorate were recorded (Figure S10). The intensity of the perchlorate peak at 932 cm^{-1} had a RSD of 10.6 %. The SERS intensity could be demonstrated by the following format:

$$I_{SERS} = N I_L |A(\nu_L)|^2 |A(\nu_S)|^2 \sigma_{ads}^R \quad (1)^{56}$$

In which I_{SERS} was the SERS intensity, N represented the molecular number involved in the SERS process, I_L was the excitation intensity, $A(\nu_L)$ and $A(\nu_S)$ were excitation and scattered field enhancement factors respectively. σ_{ads}^R was the Raman cross section of the adsorbed molecule. Assuming a, b, c … were random spots on the DDTC modified Ag/Cu fiber,

$$N_a \neq N_b \neq N_c \neq N_{\dots} \quad (2)$$

$$|A(v_L)|_a^2 |A(v_S)|_a^2 \neq |A(v_L)|_b^2 |A(v_S)|_b^2 \neq |A(v_L)|_c^2 |A(v_S)|_c^2 \neq |A(v_L)|_{\dots}^2 |A(v_S)|_{\dots}^2 \quad (3)$$

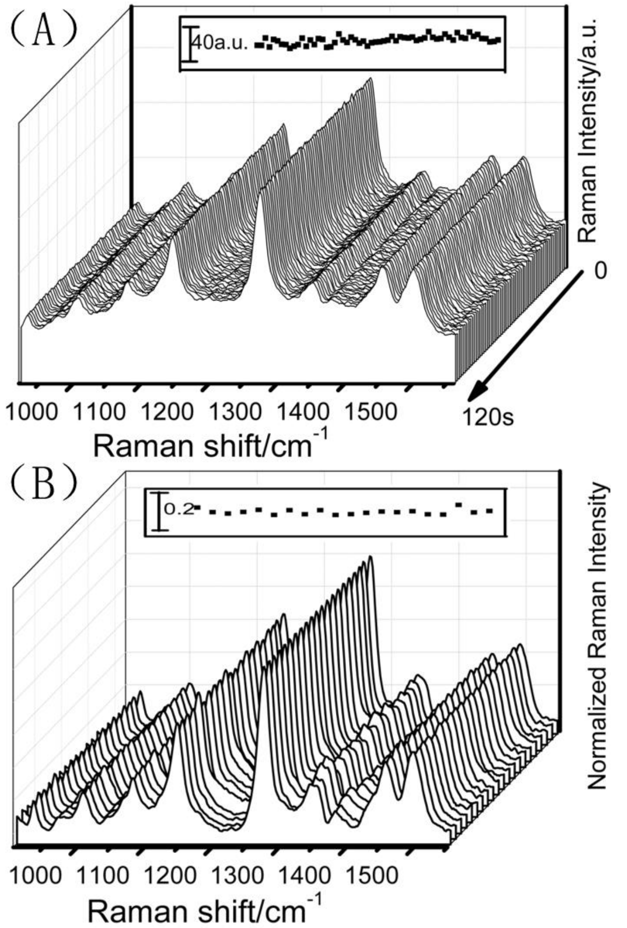


Figure 3. (A) SERS spectra of the DDTC modified Ag/Cu fiber probed with 10 μM perchlorate under continuous laser radiation. (B) The uniformity of DDTC modified Ag/Cu fiber probed with 10 μM perchlorate, the SERS spectra were normalized using the Raman peak of DDTC at 1273 cm^{-1} as the reference. Inset showed the changes of the Raman band of perchlorate at 932 cm^{-1}.

Due to the fluctuation of the Raman spectrometer, the adsorbed molecular number, the variation of the excitation and scattered field enhancement factor from spot to spot mentioned above, SERS intensity resultantly fluctuated.

$I_{SERS,\ a} \neq I_{SERS,\ b} \neq I_{SERS,\ c} \neq I_{SERS,\ \ldots}$ (4)

This case both happened to the perchlorate and DDTC. As shown in the Figure S10, the RSD of the most prominent Raman peak height signal of DDTC at 1273cm^{-1} was 12.6 %.

The excitation and scattered field enhancement factors mostly origined from surface plasmon resonances of the silver nanostructures on the fiber. At a certain spot on the DDTC modified Ag/Cu fiber, I_L, $A(\nu_L)$ and $A(\nu_S)$ were same for both perchlorate and DDTC. On the other hand, the σ_{ads}^{R} was a constant for one specific molecule. The SERS intensity of pechlorate and DDTC at each spot had a relationship as the equation (5)

$$I_{SERS}^{Normalized} = \frac{I_{SERS,ClO_4^-}}{I_{SERS,DDTC}} = k\frac{N_{ClO_4^-}}{N_{DDTC}} \quad (5)$$

Besides, the adsorption in solution usually conformed to Freundlich isotherm equation mode[49]

$$\frac{N_{ClO_4^-}}{N_{DDTC}} = k'c^{\frac{1}{n}} \quad (6)$$

In which c was the concentration of the perchlorate solution, k' and n were constant for a certain system at a certain temperature. For a specific concentration of perchlorate solution, the ratio of perchlorate to DDTC at different spots may be equal.

$$\frac{N_{ClO_4^-,a}}{N_{DDTC,a}} = \frac{N_{ClO_4^-,b}}{N_{DDTC,b}} = \frac{N_{ClO_4^-,c}}{N_{DDTC,c}} = \frac{N_{ClO_4^-,\ldots}}{N_{DDTC,\ldots}} \quad (7)$$

The Raman peak at 1273cm^{-1} assigned to the δ(HCH)(CH_3),(CH_2)[47] was selected as an internal standard peak, which was little influenced by the absorption of ClO_4^- (Table S1). Figure 3B showed the normalized SERS spectra of these 20 random points with DDTC as internal standard. A relative standard deviation of 7.2 % was shown in the inset of Figure 3B. It was obvious that normalization could diminish the fluctuation of the exciting and scattered field factor, the variation of the adsorbed perchlorate molecular number, which improved the uniformity of SERS intensity.

The reproducibility was evaluated through repeating the adsorption and elution progress. The DDTC modified Ag/Cu fiber was immersed into a 10 μM perchlorate solution for 1 hour to achieve the adsorption process. Then the fiber was immersed into the acetone solution to finish the elution process. And the SERS spectra were recorded respectively. After the elution process, the Raman peak of perchlorate at 932cm^{-1} disappeared (Figure S11), which indicated the perchlotate was rinsed by the acetone. The DDTC modified Ag/Cu fiber could still adsorb perchlorate after five cycles which had a relative standard deviation of 8.2 % (RSD of Raman peak of perchlorate at 932 cm^{-1}). This result confirmed that the DDTC modified Ag/Cu fiber had good reproducibility and the perchlorate could be detected by this DDTC modified Ag/Cu fiber repeatedly.

The investigation of extraction condition

The pH effect of perchlorate extraction

The optimum pH condition for detection of perchlorate was evaluated. The pH values from 3.0 to 11.0 were chosen to estimate the electrostatic interaction between DDTC and perchlorate. The pH value was adjusted by adding NaOH or HCl into the perchlorate solution. With the variation of the pH, the position of the perchlorate peak at 932 cm^{-1} did not change. But the Raman intensity was influenced by the pH change. Figure S12 showed that when the pH was between 5.0 and 10.0, the Raman enhanced effect was preferable and the SERS intensity of the peak at 932 cm^{-1} reached the maximum when the pH value was around 7.0. That was probably because when the pH value was higher than 10.0, the high concentration of OH$^-$ had effect on the electrostatic interaction between DDTC and perchlorate. While the pH value was lower than 5.0, the Ag nanostructure on the fiber might be destroyed which caused the decrease of the Raman intensity.[34] The pH value 7.0 was selected as the optimal pH to detect perchlorate throughout the measurement.

The interference of co-existing ion on the DDTC modified Ag/Cu fiber

The perchlorate contaminated water or soil may often contain some other anions including SO_4^{2-}, NO_3^- and Cl$^-$. To evaluate the interference of co-existing ion in the analyte solution, [41] NaCl, KNO_3, Na_2SO_4 of different concentration was adding into perchlorate solution respectively. In the meantime, the concentrations of the co-existing anion varied from 0 to 1000 μM, while the concentration of the perchlorate maintained 10 μM. They may adsorb onto the surface of the Ag/Cu fiber competing adsorption with perchlorate. Figure S13 showed the histogram of the influence for these three anions in the extraction process. The Raman intensity of the perchlorate decreased with the increasing concentration of co-existing anions. Figure S13 also showed that the interference of SO_4^{2-} was more obvious than the other two anions, probably because the highest ion strength.

The effect of extraction time

To examine the effect of extraction time on the detection, the kinetic curve of different concentration of perchlorate was investigated.[42] The DDTC-modified Ag/Cu fibers were immersed into different concentration of perchlorate solution for 500 min, recording SERS spectra every once in a while. Figure S14 showed the kinetics curves of perchlorate extraction. For perchlorate of 100, 10, 1, and 0.1 μM, the saturated extraction time was 15, 60, 120 and 360 min respectively. Hence, a relative long time of 6 h was chosen for perchlorate extraction and detection to ensure all the extraction reached equilibrium.

Quantitative detection of perchlorate

The quantitative perchlorate detection was firstly performed in purified water to evaluate the sensitivity of the Ag/Cu fiber. The perchlorate solutions in the concentration range from 0.1 to 1000 μM in purified water were prepared. Perchlorate solutions with different concentrations were extracted by the Ag/Cu fiber and the SERS spectra were recorded.

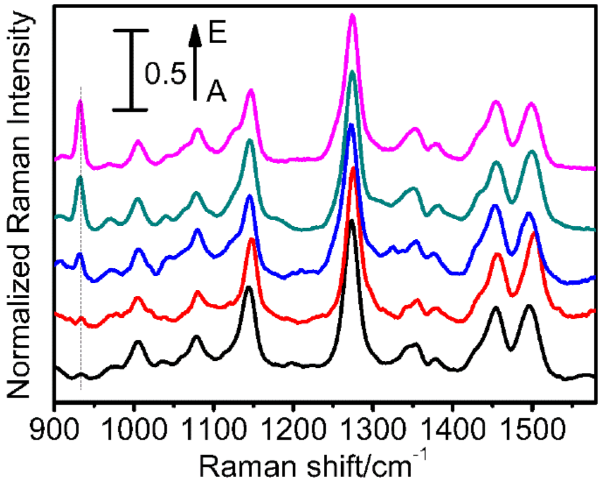


Figure 4. Normalized SERS spectra of perchlorate based on DDTC-modified Ag/Cu fiber with concentrations of (A) 0.1 μM, (B) 1 μM, (C) 10 μM, (D) 100 μM, (E) 1000 μM

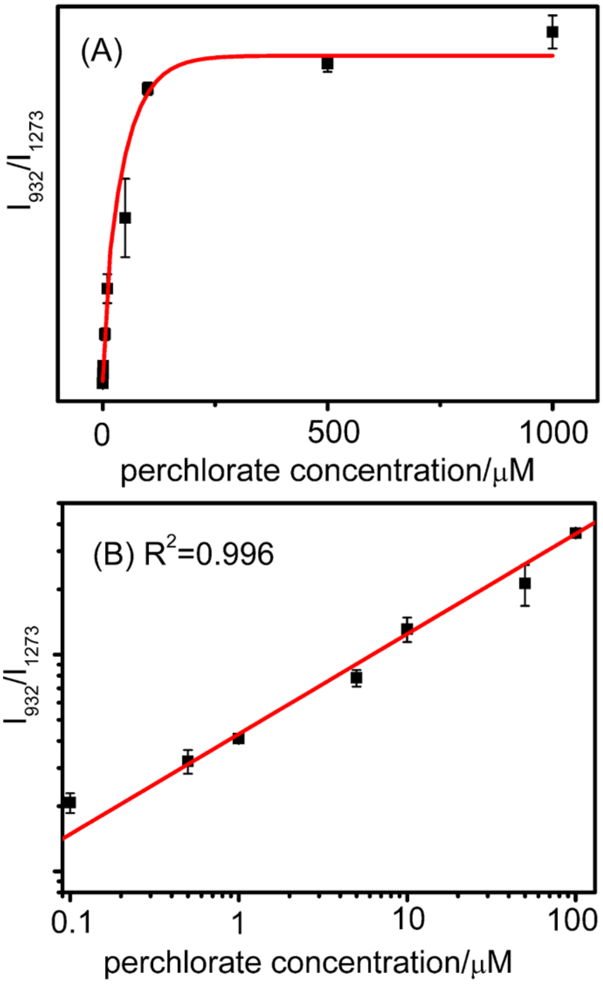


Figure 5. (A) Calibration curve and (B) log-log plot of perchlorate based on DDTC-modified Ag/Cu fiber. The data points correspond to the average of three times parallel measurements.

As shown in Figure 4, the normalized Raman intensity of perchlorate at 932cm^{-1} increased with the increasing of ClO_4^- concentrations. Quantitative SERS detection of perchlorate was also performed based on the internal reference method.[43] It could be seen from Figure 5A that the normalized intensity of the Raman peak at 932 cm^{-1} became saturate at higher concentration due to the saturation of the enhancing active sites.[52] Furthermore, the log-log plot of the normalized intensity of the Raman peak at 932 cm^{-1} versus perchlorate concentration in the range of 0.1-100 μM was obtained, which exhibited a good linear relationship as shown in the Figure 5B.

The liner equation of the fitted line was y=-1.3664+0.46196x (x is logarithm of the perchlorate concentration and y is logarithm of the normalized SERS intensity of Raman peak at 932 cm^{-1}), and the linear regression index (R^2) was 0.996. The detection limit in solution was about 6.0 ppb (SI 18, Table S2), which was determined as three times the standard deviation above the blank.

The adsorption between the DDTC modified Ag/Cu fiber and the perchlorate solution might be explained with the Freundlich isotherm equations mentioned above. The following quantitative equations were derived from the equation (5) and (6):

$$I_{SERS}^{Normalized} = k'' c^{\frac{1}{n}} \quad (8)$$

$$\log I_{SERS}^{Normalized} = \frac{1}{n}\log c + k'' \quad (9)$$

It could be inferred from this equation that the good linear relationship of the log-log plot is reasonable.

On-site detection of perchlorate in soil

First of all, pure silica sand was chosen to certify the DDTC modified Ag/Cu fiber could be used to carry out the on-site detection of perchlorate in sample matrix. 1g silica sands was weighed and transferred into the containers. They were spiked 0.5 ml different concentrations of perchlorate solution, which immersed the whole sands. After one night diffusion, the perchlorate was dispersed throughout the silica sands. A stirring rod was used to stir the mixture to make them more homogeneous. The DDTC modified Ag/Cu fibers were directly immersed into the sand and the extraction was performed at ambient temperatureat for 6 hours.

Then the DDTC modified Ag/Cu fiber was taken out and washed with ultrapure water to move the residual silica sands on the fiber away. Then the fiber was taken to the Raman spectra for SERS detection. As Figure S15 showed, perchlorate in the silica sand had been extracted and quantitative detected. The detection limit in silica sands was 0.035 ppm, which was determined as three times the standard deviation above the blank.

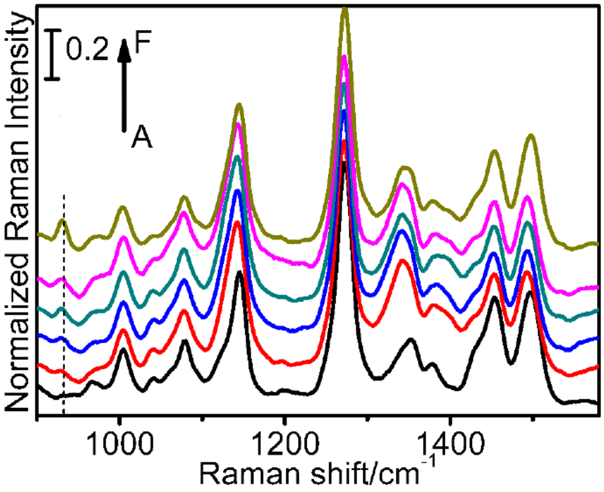


Figure 6. Normalized SERS spectra for the direct detection of perchlorate in real soil by the DDTC-modified Ag/Cu fiber with concentration of (A) 0 ppm (B) 0.5ppm (C) 1.0 ppm (D) 5.0 ppm (E) 10ppm (F) 50ppm. (10^{-6} g/g soil dry weight)

Technique	Recovery (%)	RSD (%)
IC	95	1.8
LC/MS/MS[50]	121	6.4
Our method	105	4.7

Table 1. Comparison of the analytical performance of various methods for determination of perchlorate in soil.

The DDTC modified Ag/Cu fiber was also suitable for perchlorate in real soil directly without preparing soil extractant solutions. The collected soil was dried and sieved in advance for further use. Then the experimental procedure was performed similar to that performed in silica above. In order to realize the on-site detection in perchlorate contaminated soil or slurries, direct solid phase microextraction was also preferred to extract perchlorate in the water-soil (slurries).[57-59] Thus, the content of perchlorate could be estimated in field without much more sample pretreatment. The detection result was shown in Figure 6. The detection of perchlorate with ion chromatography of the real sample was also carried out for comparison as shown in Figure S16. The detection limit was 0.081 ppm in real soil (SI8, Table S2). The performance of recovery for real soil samples of this method was also satisfied, which was compared with LC/MS/MS and IC. The analytical performances were listed in Table 1.

Conclusions

In this work, a SERS-active DDTC modified Ag/Cu fiber was fabricated to extract and on-site detect perchlorate using a portable Raman spectrometer. An Ag/Cu fiber was fabricated through the modified galvanic displacement, and the DDTC was used as the modifier which played a dual role in the process: preconcentration of perchlorate close to the fiber surface through their electrostatic interaction and acting as an internal spectral reference in the quantitative detection. The log-log plots of SERS intensity versus the perchlorate concentration showed good linear relationship in the concentration range from 0.1 to 100 μM. Compared to the conventional SERS detection previously, using this DDTC modified Ag/Cu fiber, the perchlorate could be not only detected in solution but also directly extract and detect perchlorate in the polluted soil free from complex sample pretreatment. The detection limit in soil (0.081 ppm) is lower than the EPA regulation of the perchlorate safety standard. The detection results were comparable with that obtained from ion chromatography. This hyphenated method of microextraction with direct SERS detection may find potential application for direct pollutants detection free from pretreatment.

Acknowledgements

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Supporting information

The SI includes 16 figures and one table. This material is available free of charge via the Internet at http://pubs.acs.org.

Notes and references

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† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/.

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