

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

*Sha Zhu, Xiaoli Zhang, Jingcheng Cui, Yu-e Shi, Xiaohong Jiang, Zhen Liu, Jinhua Zhan**

Key Laboratory of Colloid and Interface Chemistry, Ministry of Education,
Department of Chemistry, Shandong University, Jinan 250100, China

*Address for correspondence. Email: jhzhan@sdu.edu.cn

Phone: 86-531-88365017; Fax: 86-531-88366280

1. XRD patterns of the Ag/Cu fiber before and after the modification.
2. SEM images of the Ag/Cu fiber before and after the modification.
3. Structures of DDTC before and after modification.
4. Elemental sulfur representation of the DDTC modified Ag/Cu fiber.
5. Investigation of the concentration of DDTC in the modification process.
6. Investigation of the immersion time of DDTC in the modification process.
7. SERS spectra of the DDTC modified Ag/Cu fiber and the Raman spectrum of perchlorate powder.
8. SERS spectrum of perchlorate extracted on the DDTC modified Ag/Cu fiber compared with the Raman spectrum of the perchlorate powder.

9. Perchlorate detection before and after modification of DDTC.
10. The SERS spectra of the uniformity measurements of DDTC modified Ag/Cu fiber probed with 10^{-5} M perchlorate.
11. Selection of internal standard Raman peak.
12. The reusability of DDTC modified Ag/Cu fiber.
13. The pH effect of perchlorate extraction.
14. The interference of co-existing ion on the DDTC modified Ag/Cu fiber.
15. The effect of extraction time
16. Normalized SERS spectra of perchlorate detection in silica sands by the DDTC-modified Ag/Cu fiber with different concentrations.
17. Perchlorate in soil detected by Ion Chromatography.
18. The LOD (Limit of Detection) in water and soil samples.

1. XRD patterns of Ag/Cu fiber before and after the modification.

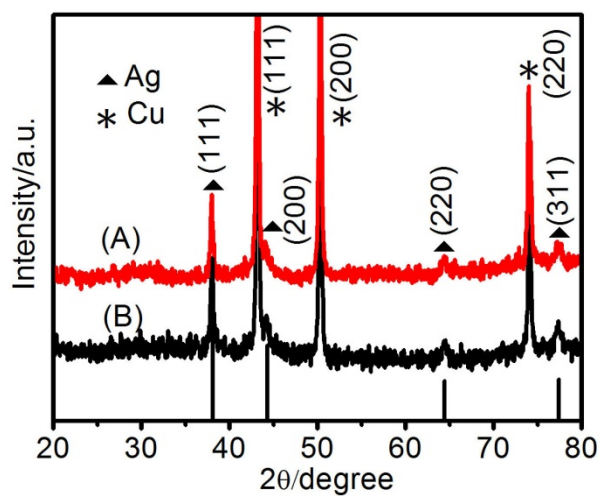
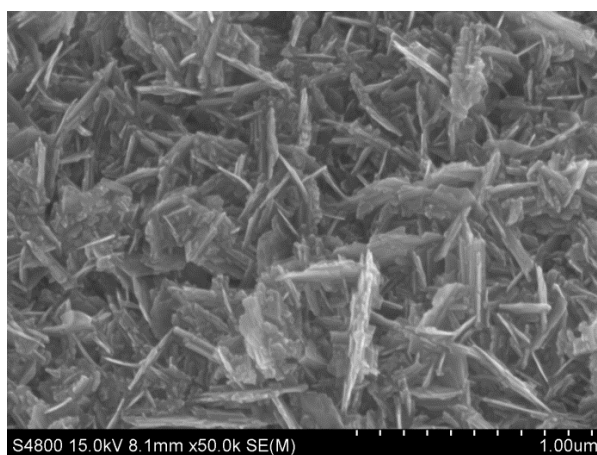
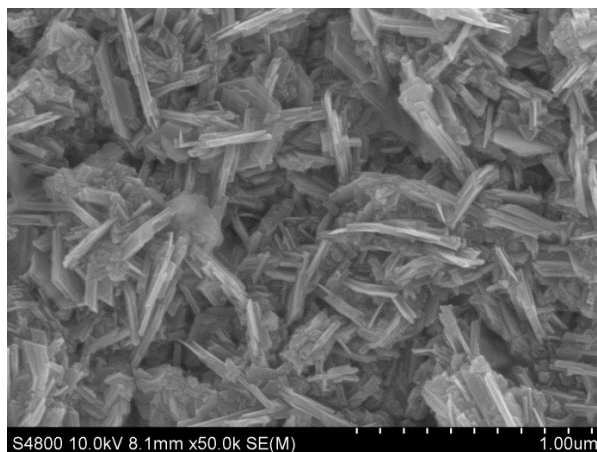


Figure S1. XRD patterns of the Ag/Cu fiber (A) before and (B) after it was modified with DDTC.

2. SEM images of Ag/Cu fiber before and after the modification.



(A)



(B)

Figure S2. SEM images of the Ag/Cu fiber (A) before and (B) after it was modified with DDTC.

3. Structures of DDTC before and after modification.

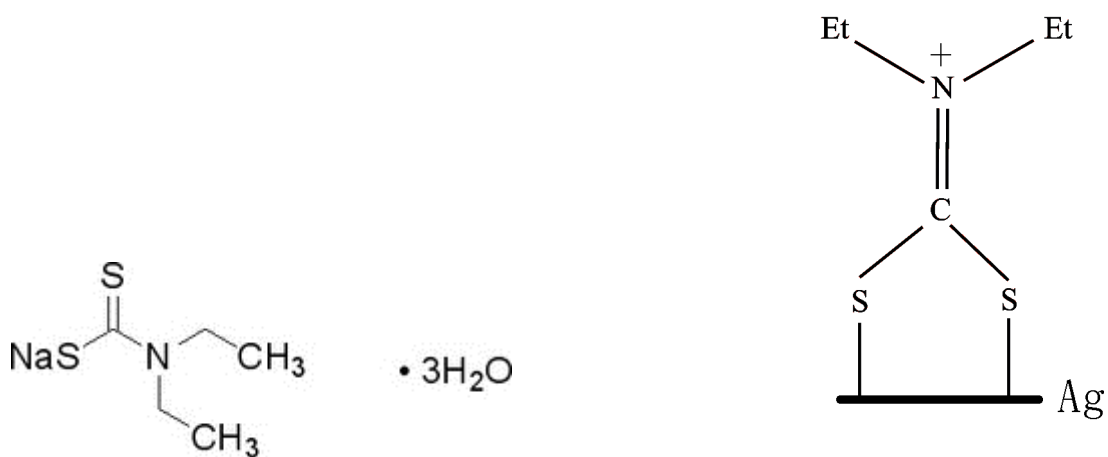


Figure S3. Structures of DDTC before and after modified on the silver nanoplates.

4. Elemental sulfur representation of the DDTC modified Ag/Cu fiber.

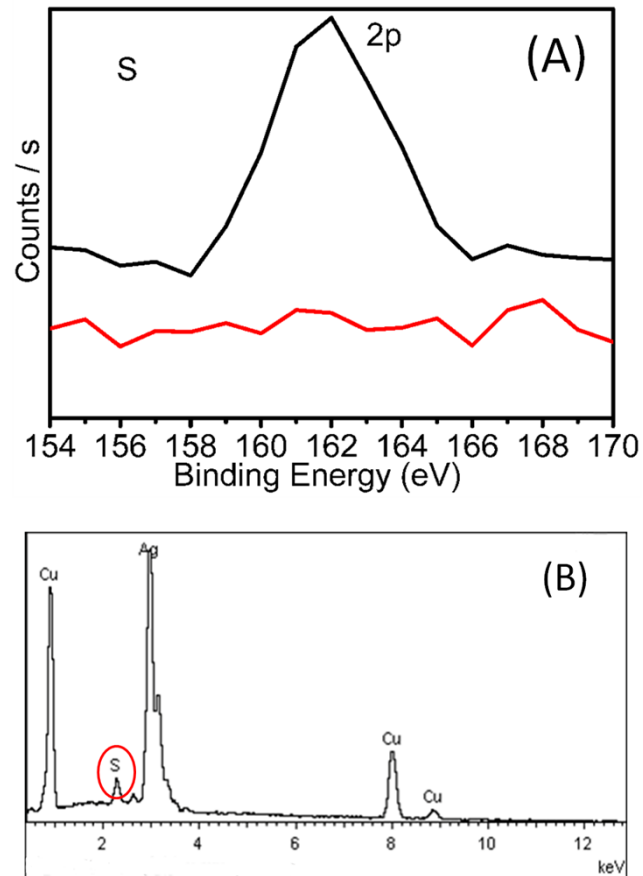
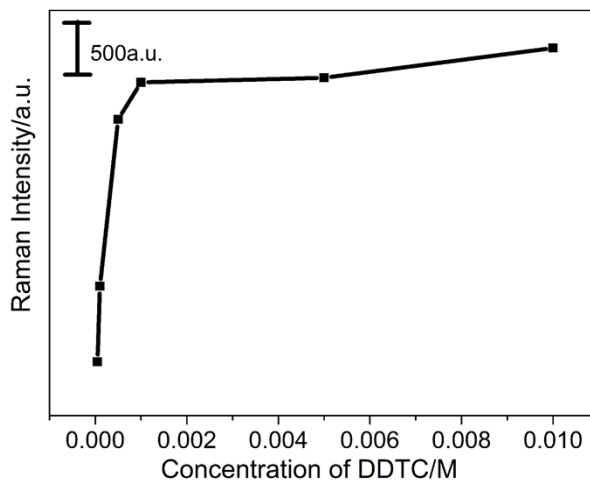
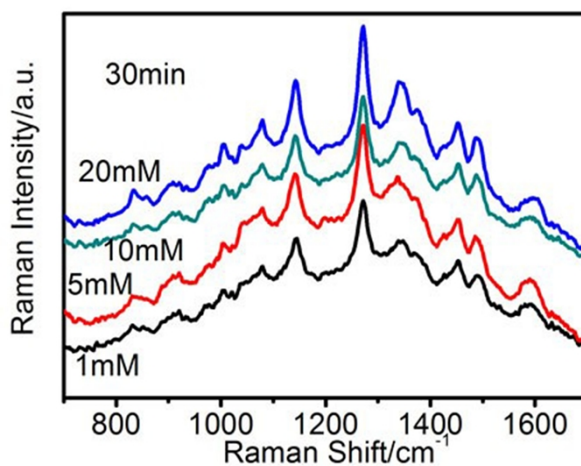


Figure S4. (A) The XPS representation of the binding energy of S (2p) at 162 eV after modification. (B) EDS of the DDTc modified Ag/Cu fiber.

5. Investigation of the concentration of DDTc in the modification process.



(A)

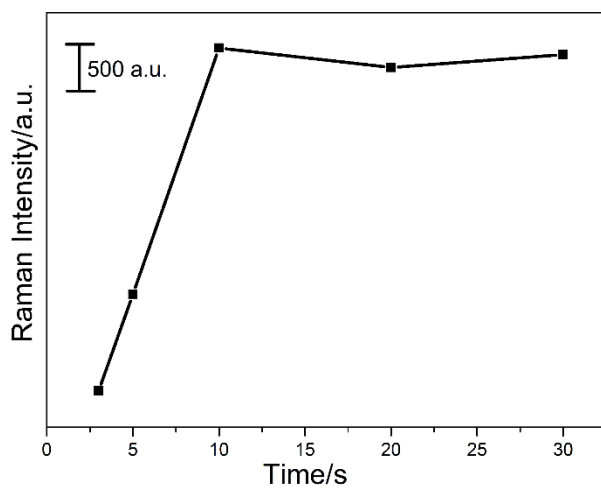


(B)

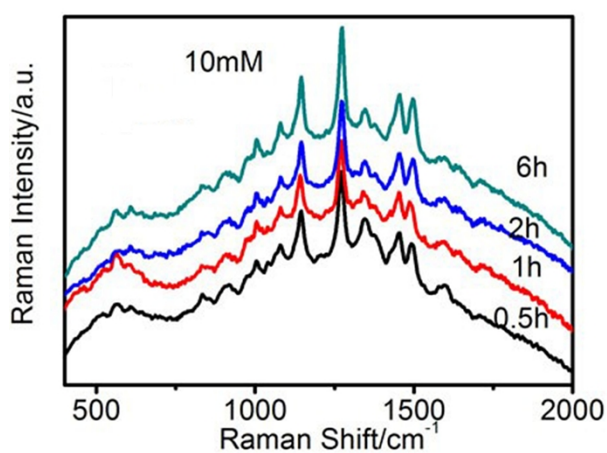
Figure S5. (A) Variation of SERS intensity of DDTC with different concentrations of 0.05 mM, 0.1 mM, 0.5 mM, 1mM, 5 mM,10 mM. (B) SERS spectra of the fiber immersed in different saturated concentrations of DDTC for 30 min.

Figure S5 (A) showed that the adsorption of DDTC had reached saturation with a concentration of 1mM (30 min). Figure S5 (B) confirmed that the SERS intensity scarcely changed with the variation of its concentration when the modification was saturated.

6. Investigation of the immersion time of DDTC in the modification process.



(A)



(B)

Figure S6. (A) Variation of SERS intensity of DDTC with the different immersion time of 3 min, 5 min, 10 min, 20 min, 30 min. (B) SERS spectra of the fiber immersed in 10 mM DDTC for different saturated time.

Figure S6 (A) showed that the adsorption of DDTC (10 mM) had reached saturation within 10 min. Figure S6 (B) confirmed that the SERS intensity scarcely changed with the variation of immersion time when the modification was saturated.

7. SERS spectra of the DDTC modified Ag/Cu fiber and The Raman spectrum of perchlorate powder.

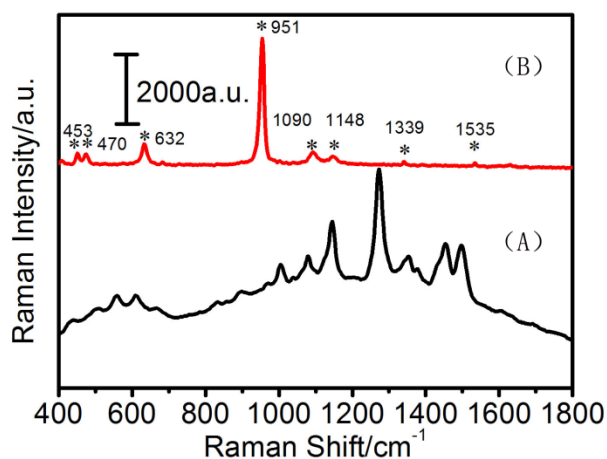


Figure S7. (A) SERS spectrum of the DDTC modified Ag/Cu fiber and (B) The Raman spectrum of perchlorate powder for comparison.

8. SERS spectrum of perchlorate extracted on the DDTC modified Ag/Cu fiber compared with the Raman spectrum of the perchlorate

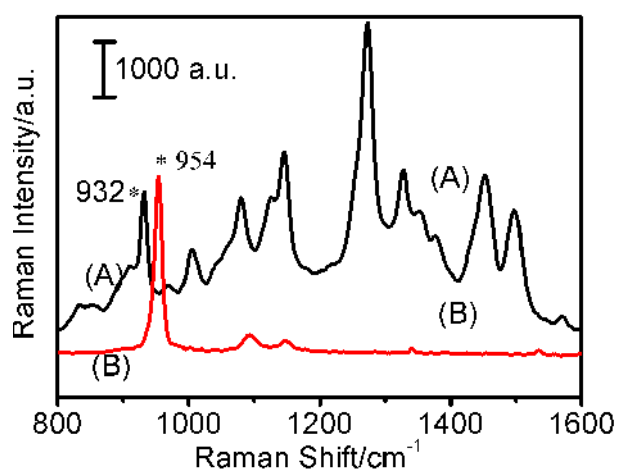


Figure S8. (A) SERS spectrum of perchlorate extracted on the DDTC modified Ag/Cu fiber and (B) the Raman spectrum of perchlorate for comparison.

9. Perchlorate detection before and after modification of DDTC.

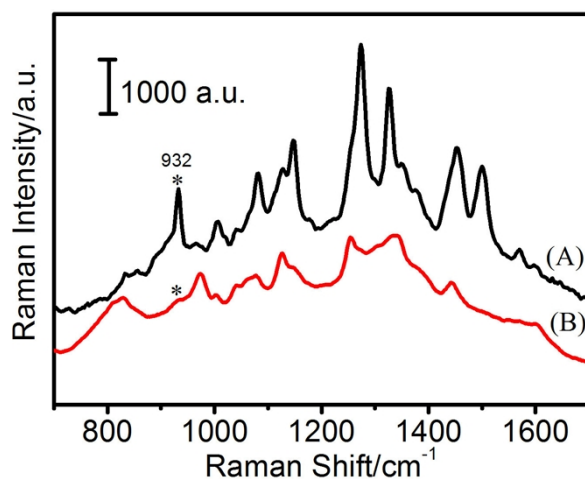


Figure S9. SERS spectra of detection of perchlorate (A) after and (B) before the modification of DDTC on the Ag/Cu fiber.

10. The SERS spectra of the uniformity measurements of DDTC modified Ag/Cu fiber probed with $10 \mu\text{M}$ perchlorate.

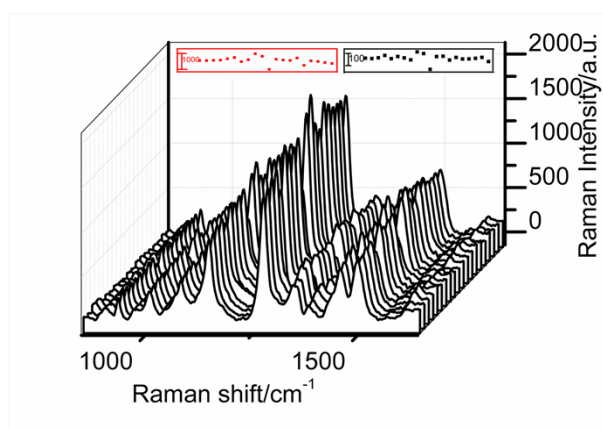


Figure S10. The SERS spectra of the uniformity measurements of DDTC modified Ag/Cu fiber probed with $10 \mu\text{M}$ perchlorate. Inset represented the Raman intensity change of Raman band at 932 cm^{-1} (black), the Raman intensity change of Raman band at 1273 cm^{-1} (red).

11. Selection of internal standard Raman peak.

Raman peak position	1273cm ⁻¹	1497cm ⁻¹
Vibrational mode	$\delta(\text{HCH})(\text{CH}_3)$, (CH ₂)	$\nu_{\text{as}}(\text{C}=\text{N}) + \delta(\text{HCH})(\text{CH}_2)\text{sciss.}$
R ²	0.996	0.969

Table S1. comparison of linear regression index (R²) with different internal standard.

In our previous report, the normalized Raman intensity versus its concentration exhibits a log-log linear correlation. R² was the linear regression index of the log-log plots with different internal standard Raman peak, which reflected the linear correlation degree. The Raman peak at 1273cm⁻¹ was superior to be chosen as the internal standard than the Raman peak at 1497cm⁻¹ that assigned to the $\nu_{\text{as}}(\text{C}=\text{N})$, owing to the fact that the $\nu_{\text{as}}(\text{C}=\text{N})$ may be influenced by the ClO₄⁻ adsorption process.

12. The reusability of DDTC modified Ag/Cu fiber.

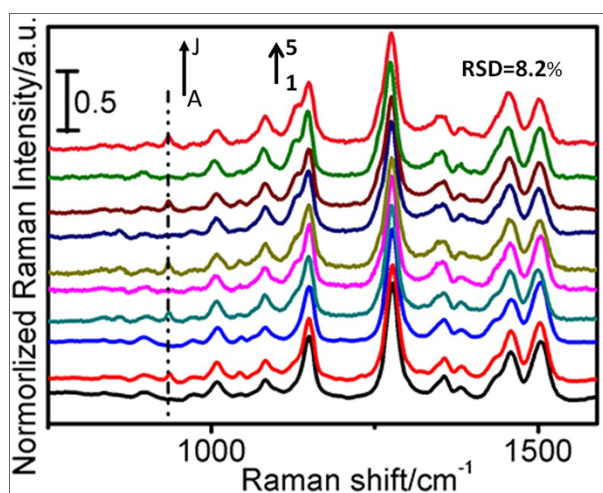


Figure S11. The reusability of DDTC modified Ag/Cu fiber. (A), (C),(E),(G) and (I) The Ag/Cu fiber was immersed in 10 μM perchlorate for 1 hour.(B),(D),(F),(H) and (J) The DDTC modified Ag/Cu fiber was rinsed with acetone. All the SERS spectra were normalized by the Raman peak of DDTC at 1273 cm^{-1} as the reference.

13. The pH effect of perchlorate extraction

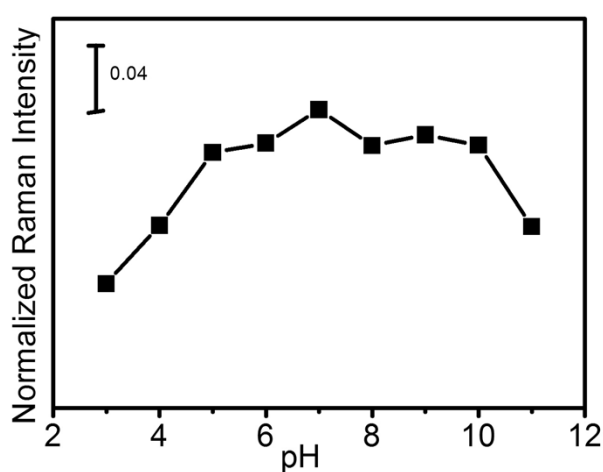


Figure S12. plot of normalized intensity of perchlorate at 932 cm^{-1} with the concentration of 10 μM against the pH from 3.0 to 11.0 on DDTC modified Ag/Cu fiber respectively.

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

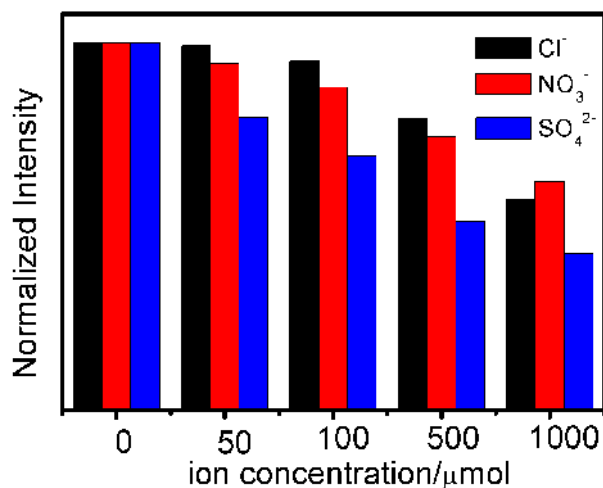


Figure S13. Effect of inorganic salt ions Cl^- , NO_3^- , SO_4^{2-} concentration on the detection of perchlorate. The initial perchlorate concentration was $10 \mu\text{M}$.

15. The effect of extraction time

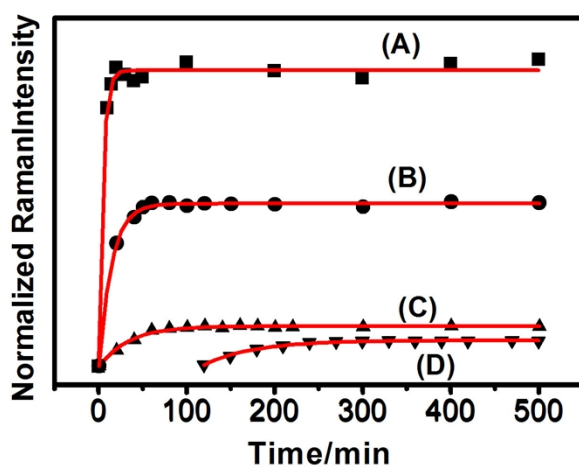
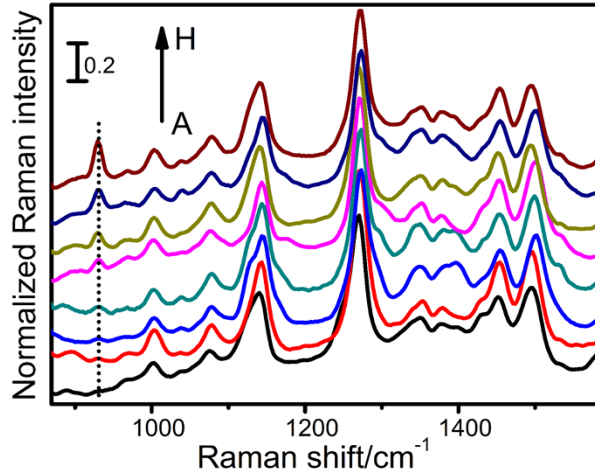
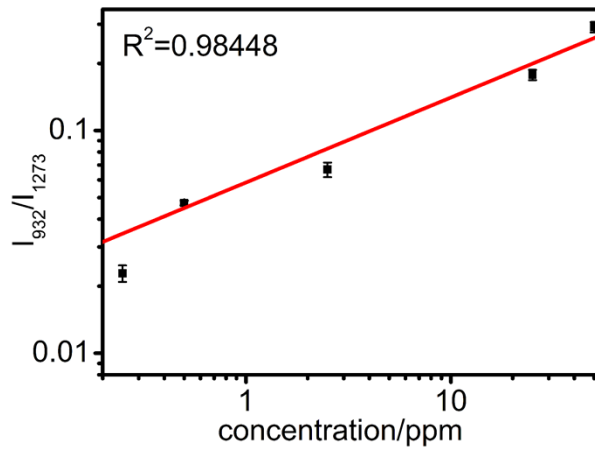


Figure S14. Kinetic curve of (A) $100 \mu\text{M}$ (B) $10 \mu\text{M}$, (C) $1 \mu\text{M}$ (D) $0.1 \mu\text{M}$ perchlorate extraction onto the DDTC-modified Ag/Cu fiber.

16. Normalized SERS spectra of perchlorate detection in silica sands by the DDTC-modified Ag/Cu fiber with different concentrations.



(a)

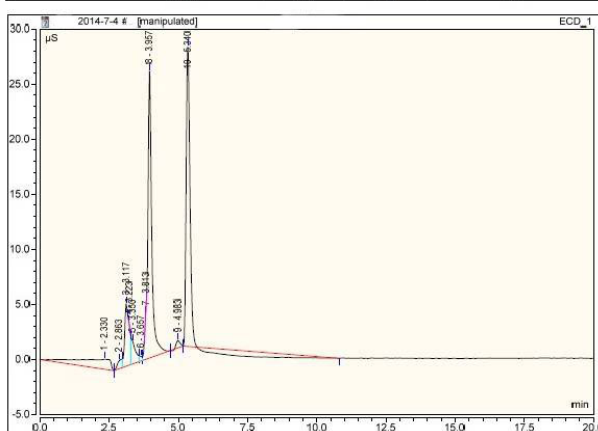


(b)

Figure S15. (a) Normalized SERS spectra of perchlorate detection in silica sands by the DDTC-modified Ag/Cu fiber with concentrations of (A) 0 ppm (B) 0.050 ppm, (C) 0.25 ppm, (D) 0.50 ppm, (E) 2.5 ppm, (F) 5.0 ppm (G) 25 ppm (H) 50 ppm.(b) log-log plot of perchlorate detection in silica sands. The data points correspond to the average of three times parallel measurements.

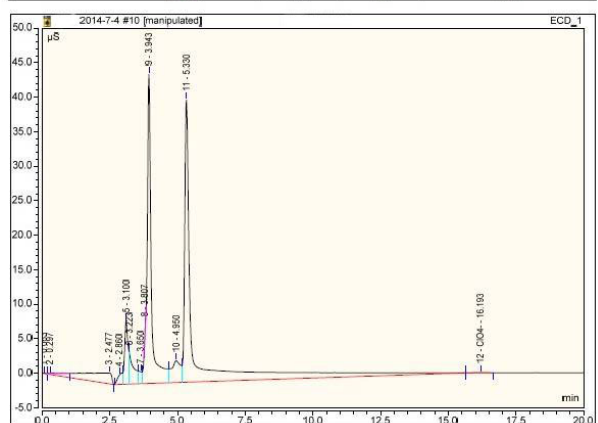
17. perchlorate in soil detected by Ion Chromatography

No.	Time min	Peak Name	Peak Type	Area • S*min	Height • S	Amount n.a.
TOTAL:				0.00	0.00	0.00



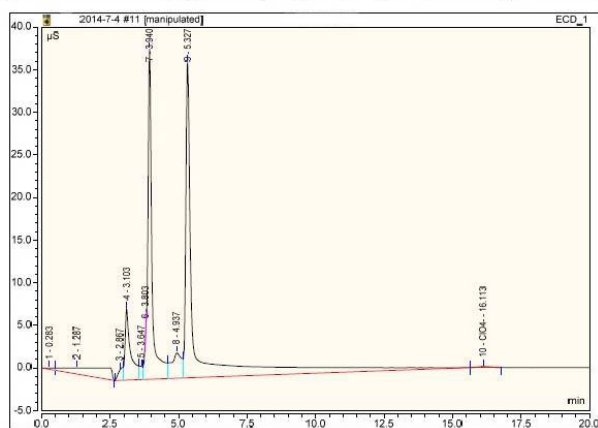
(A)

No.	Time min	Peak Name	Peak Type	Area • S*min	Height • S	Amount
12	16.19	ClO ₄ ⁻	MB*	0.028	0.058	0.1201
TOTAL:				0.03	0.06	0.12



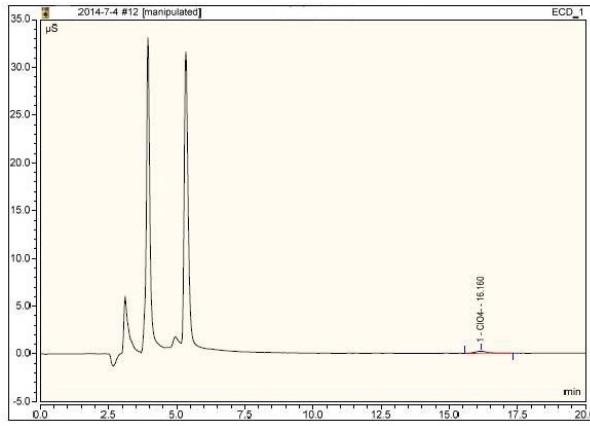
(B)

No.	Time min	Peak Name	Peak Type	Area • S*min	Height • S	Amount
10	16.11	ClO ₄ ⁻	bMB*	0.060	0.130	0.2479
TOTAL:				0.06	0.13	0.25



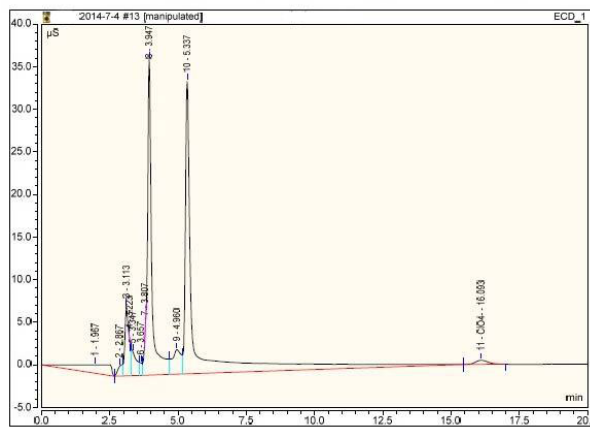
(C)

No.	Time min	Peak Name	Peak Type	Area * S/min	Height * S	Amount
1	16.16	ClO4-	BMB*	0.112	0.210	0.4585
TOTAL:				0.11	0.21	0.46



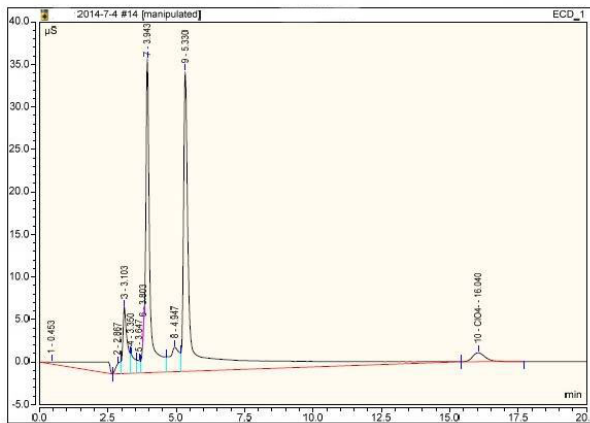
(D)

No.	Time min	Peak Name	Peak Type	Area * S/min	Height * S	Amount
11	16.09	ClO4-	bMB*	0.252	0.484	1.0150
TOTAL:				0.25	0.48	1.02

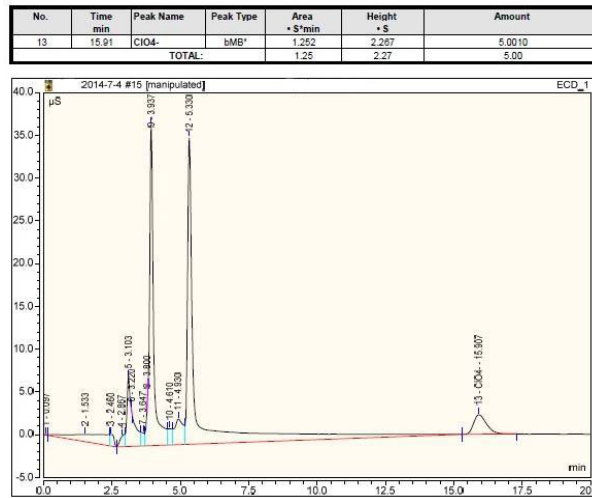


(E)

No.	Time min	Peak Name	Peak Type	Area * S/min	Height * S	Amount
10	16.04	ClO4-	bM*	0.583	1.047	2.3337
TOTAL:				0.58	1.05	2.33



(F)



(G)

Figure S16. Ion Chromatography of perchlorate in soil extract samples with concentration of (A) 0 mg/L (B) 0.12 mg/L(C) 0.25 mg/L (D) 0.50 mg/L (E) 1.0 mg/L (F) 2.5 mg/L (G) 5.0 mg/L

18. The LOD (Limit of Detection) in water and soil samples.

LOD was determined as three times the standard deviation above the blank.

$y = \text{three times the standard deviation above the blank.}$

$x = \text{limit of detection (LOD).}$

	standard deviation	linear equation	LOD
water	0.00393	Logarithm $y = -1.3664 + 0.46196$ logarithm x	6.0 ppb
soil	0.00400	Logarithm $y = -1.56717 + 0.32373$ logarithm x	0.081 ppm

Table S2. The LOD in water and soil samples.