Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary Information for

Diethyldithiocarbamate (DDTC) induced formation of positively charged silver nanoparticles for rapid in-situ identification of inorganic explosives by surface enhanced Raman spectroscopy

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1. The EDS of the DDTC modified silver colloid and the XPS spectra of the S (2p) scan of silver colloid after modification with DDTC.
2. Experimental Raman peaks for DDTC powder and SERS peaks for DDTC modified silver nanoparticles.
3. Structures of DDTC before and after modification.
4. Chemical structures of three explosives characteristic anions.
5. The pH effect of DDTC modification.
6. SEM image of the silver colloid.
7. The discrepancy of aggregated and nonaggregated DDTC modified silver nanoparticles.
8. Investigation of the volume of DDTC in the modification process.
9. SERS spectra of explosives anions extracted on the DDTC modified Ag/Cu fiber compared with the Raman spectra of the explosives anions powder.
10. The explosives anions detection before and after modification of DDTC.
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1. The EDS of the DDTC modified silver colloid and the XPS spectrum of the S (2p) scan of silver colloid after modification with DDTC.

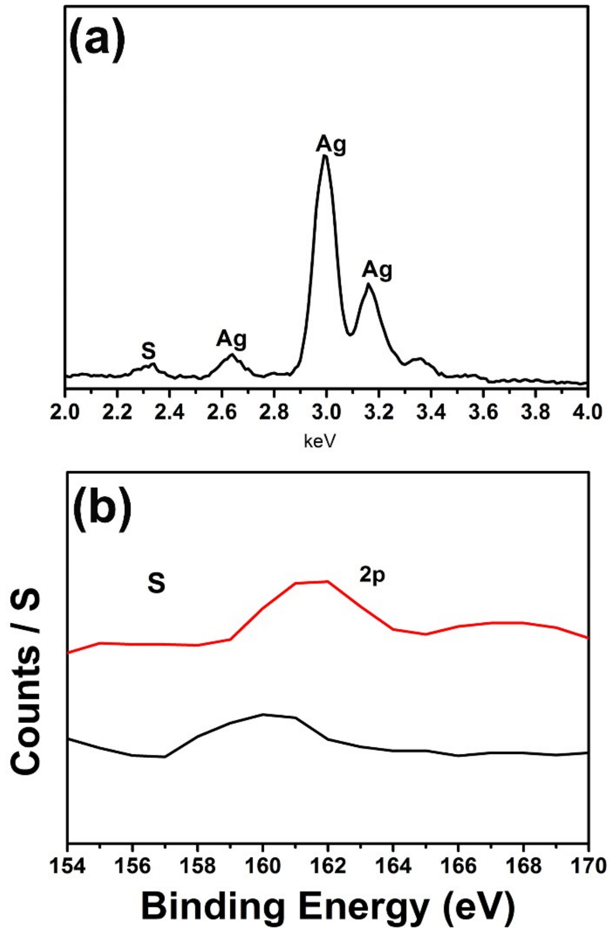

Figure S1. (a) EDS of the DDTC modified silver colloid. (b) XPS spectra of the S (2p) scan of the silver colloid before (red) and after (black) modification with DDTC.

2. Experimental Raman peaks for DDTC powder and SERS peaks for DDTC modified silver nanoparticles.

Table S1 SERS and Normal-Raman bands of DDTC with their assignments[1-3]. Wavenumbers in cm^{-1}.

SERS (cm^{-1})	Normal-Raman (cm^{-1})	Approximate assignment
-	310	N–C=S in plane bending
-	423	S=C–S stretch
564	568	NCS2 out of plane wagging
776	775	CCNC stretch
-	835	CH_3 rock; CH_2 rock
894	914	CH_3 rock; CH_2 rock
1003	1006	CH symmetrical twist
1074	1074	CS2 antisymmetric stretch
1145	1135	CH_3 rock; CH_2 rock
1273	1267	CH anti-symmetrical clipping
1374	1370	CH symmetrical wagging
1423	1417	CH symmetrical clipping
1497	-	ν (C=N) and δ(HCH)(CH2) sciss

3. Structures of DDTC before and after modification.

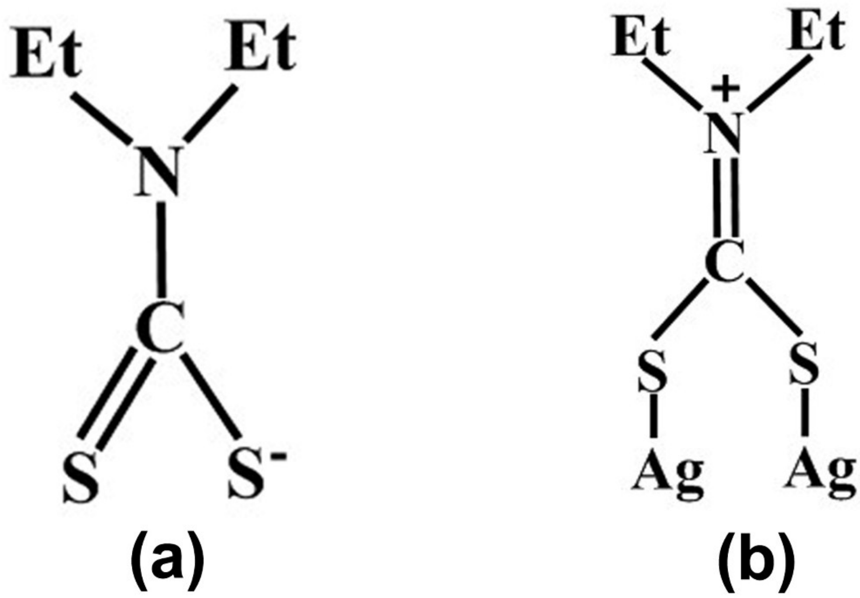

Figure S2.Structures of DDTC before and after modified on the sliver nanoparticles.

4. Chemical structures of three explosives characteristic anions.

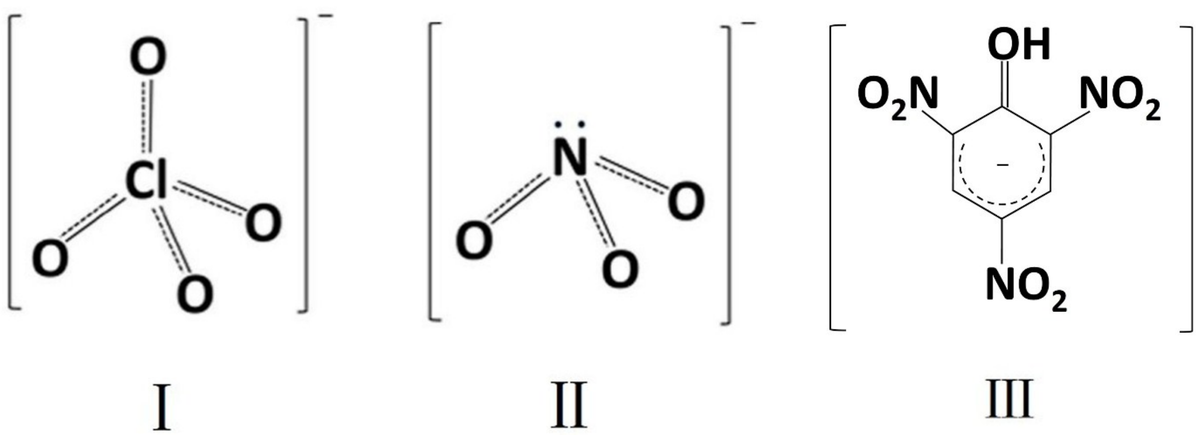

Figure S3. Chemical structures of (Ⅰ) perchlorate (ClO_4^-), (Ⅱ) nitrate (NO_3^-) and (Ⅲ) picric acid (PA)

5. The pH effect of DDTC modification.

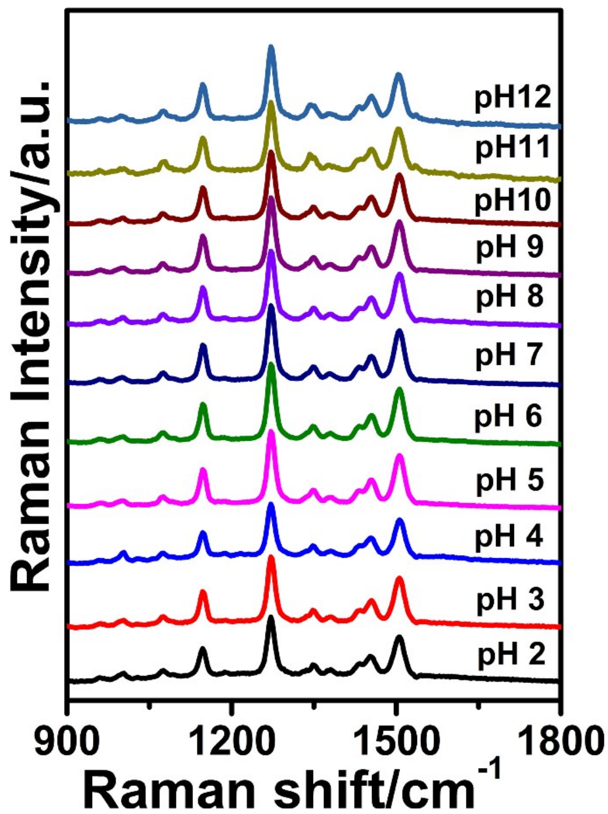

Figure S4 Raw Raman spectra of DDTC-silver colloid at varying pH values. The pH was adjusted using HCl or NaOH.

6. SEM image of the silver colloid.

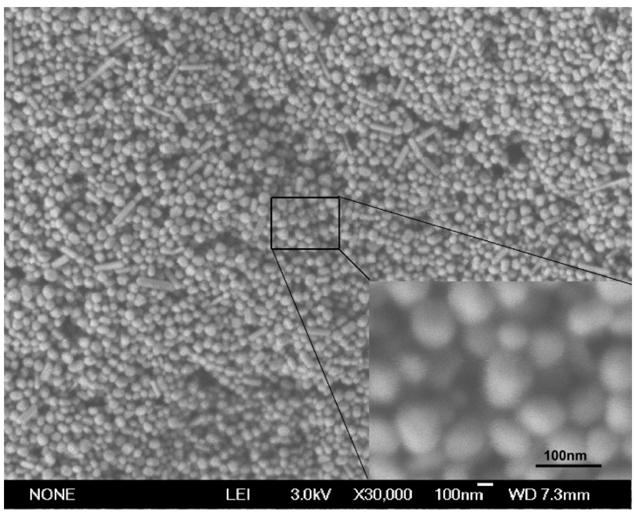

Figure S5. SEM image of the evaporated DDTC-modified silver colloid.

7. The discrepancy of aggregated and non-aggregated DDTC modified silver nanoparticles.

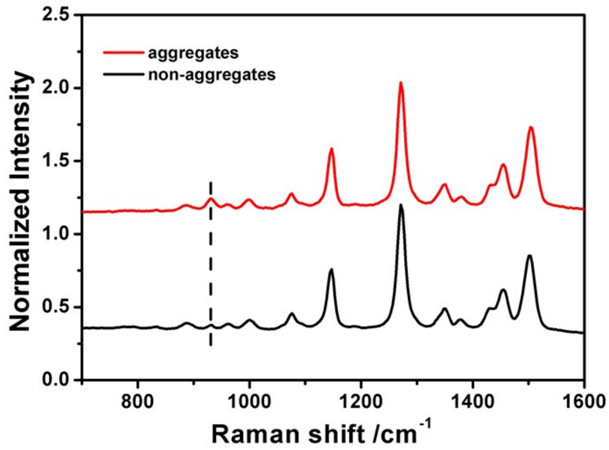

Figure S6. SERS spectra of 0.1 mM perchlorate with aggregated DDTC modified silver nanoparticles (red) and non-aggregated DDTC modified silver nanoparticles (black).

8. Investigation of the volume of DDTC in the modification process.

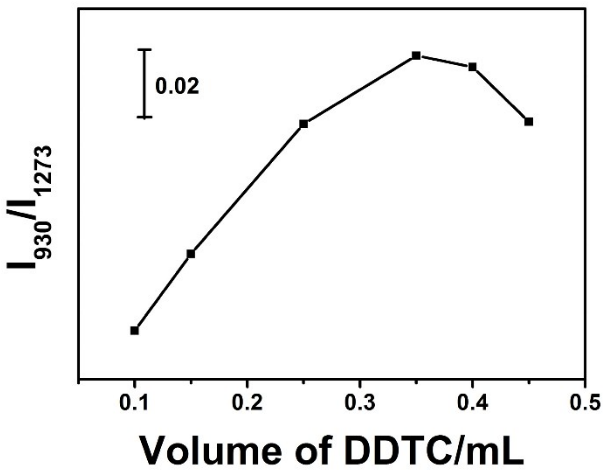

Figure S7. Plot of normalized intensity of perchlorate at 930 cm^{-1} with the various volume of DDTC modified silver colloid. The volume of DDTC is 0.10mL, 0.15 mL, 0.25 mL, 0.35 mL, 0.4 mL, 0.45 mL respectively.

9. SERS spectra of explosives anions extracted on the DDTC modified Ag nanoparticles compared with the Raman spectra of the explosives anions powder.

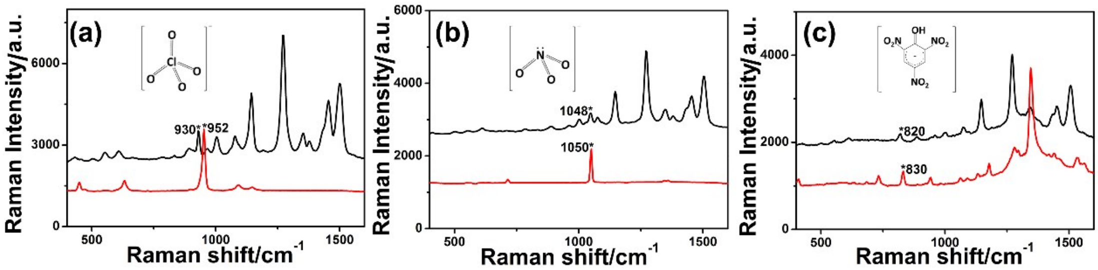

Figure S8. SERS spectra of detection of perchlorate (a), nitrate (b) and PA (c) (black) and the Raman spectra of perchlorate (a), nitrate (b) and PA (c) powder (red) for comparison.

10. The explosives anions detection before and after modification of DDTC.

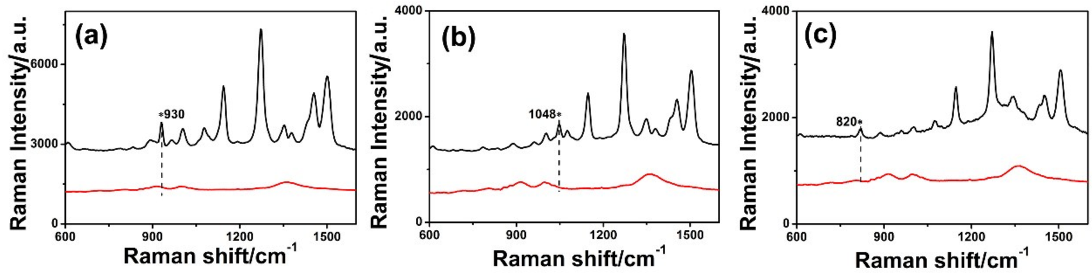

Figure S9. SERS spectra of detection of perchlorate (a), nitrate (b) and PA (c) after (black) and before (red) the modification of DDTC on the silver colloid.

11. The uniformity of DDTC-modified silver colloid before and after normalization.

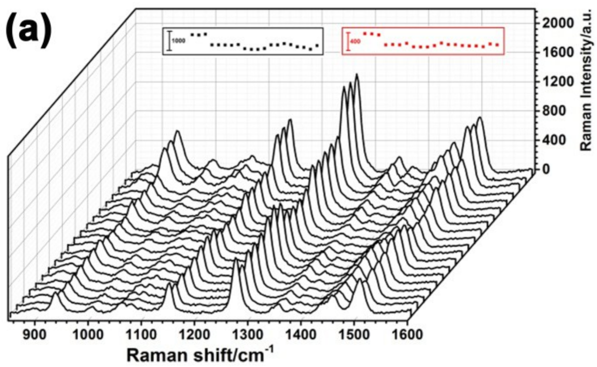

Figure. S10a. The uniformity before normalization of DDTC-modified silver colloid on the tin foil probed with 1 mM perchlorate, Inset represented the Raman intensity change of Raman band of perchlorate at 930 cm^{-1} (red) with an RSD of 11.4% and the Raman intensity change of Raman band of DDTC at 1273 cm^{-1} (black) with an RSD of 14.4%.

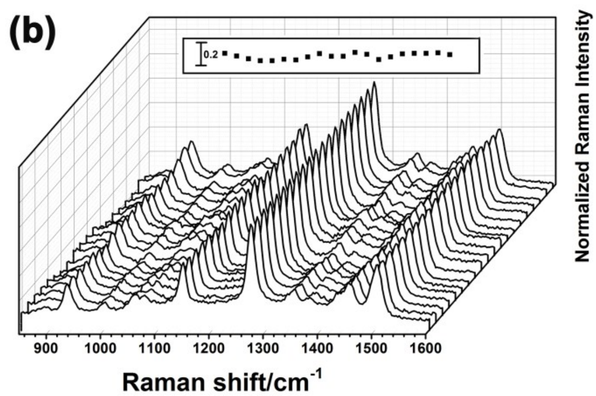

Figure. S10b. The uniformity after normalization of DDTC-modified silver colloid on the tin foil probed with 1 mM perchlorate. The SERS spectra were normalized using the Raman peak of DDTC at 1273 cm^{-1} as the reference. Inset shows the changes of the Raman band of perchlorate at 930 cm^{-1} with an RSD of 5.45%.

12. Reproducibility study.

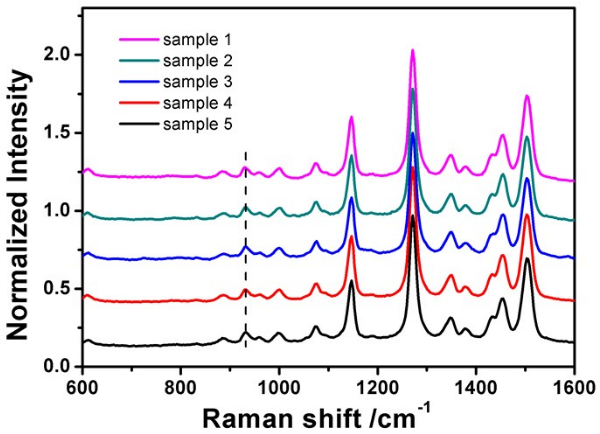

Figure .S11 SERS spectra of five sample of 0.1 mM perchlorate.

13. The study of ageing time of the DDTC modified silver nanoparticles.

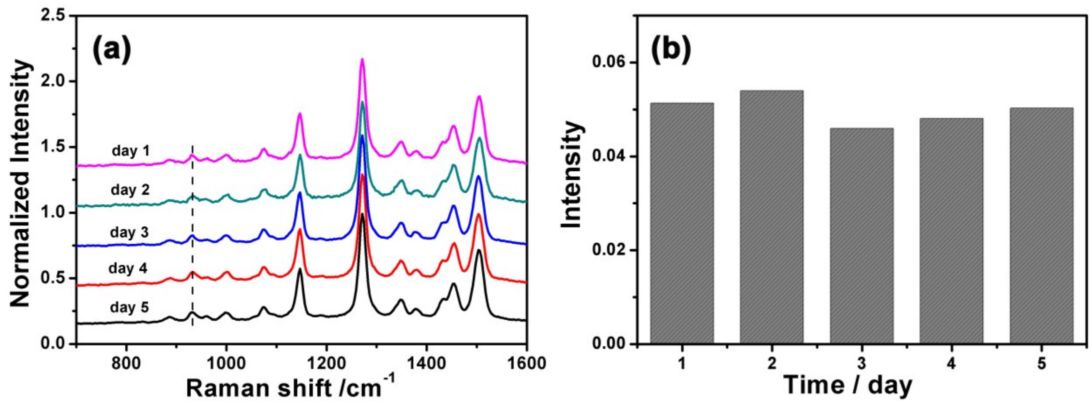

Figure. S12 (a)SERS spectra of 0.1 mM perchlorate with DDTC modified silver colloid of storage time; (b) the normalized Intensity at 930 cm^{-1} over 5 days.

14. The calculated EFs of three explosives characteristic anions.

Table S2 EF (Enhancement factor) of anions

	perchlorate	nitrate	picric acid
EF	2.5×10^4	2.3×10^4	2.1×10^4

The enhancement factor (EF) also calculated using the formula:[4]

$$EF = (I_{SERS}/I_{Raman}) \cdot (N_{bulk}/N_{ads})$$

where I_{SERS} is the intensity of surface enhanced signal (at lower concentration), N_{ads} is the number of explosives anions under laser radiation adsorbed on substrate, I_{Raman} is the intensity of normal Raman signal of explosives anion powders, and N_{bulk} is the number of explosives anions in the scattering volume in bulk solution.

15. Preparation and Raman characterization of DDTC induced the positively charged gold nanoparticles.

Citrate stabilized Au NPs were prepared according to the kinetically controlled seeded growth method.[5] The positively charged gold colloid was obtained by modifying with DDTC similar to the silver colloid.

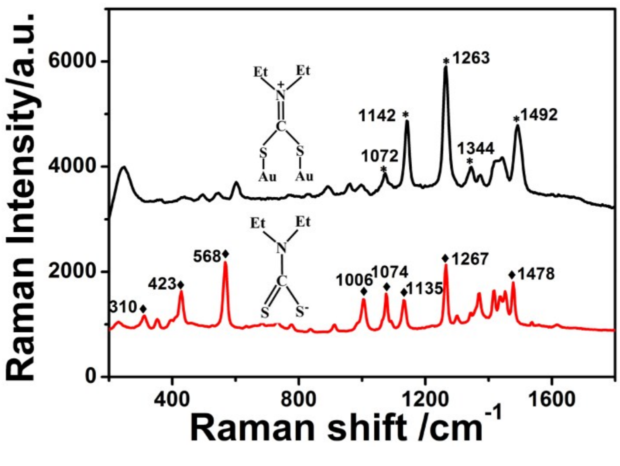

Figure. S13 Raman spectra of DDTC powder (red) and DDTC modified on the gold colloid (black).

16. The analytical performance of various methods for inorganic explosives determination.

Table S3. Comparison of the analytical performance of various methods for inorganic explosives determination

	IC[6]	CE[7]	IMS[8]	Our method
ClO_4^-	8.4 ppb	0.90 mg/L	6.30 ng	1.19 ng/cm^2
NO_3^-	5.4 ppb	0.57 mg/L	0.10 ng	2.01 ng/cm^2

LOD was determined as three times the standard deviation above the blank.
y=three times the standard deviation above the blank.
x= limit of detection (LOD).

Anions	perchlorate	nitrate	picric acid
Liner equation	$y=4.73\times10^{-3}+1.84\times10^{-4}x$	$y=4.44\times10^{-3}+2.73\times10^{-4}x$	y=3.00×10-3+2.34×10-4x
Standard	0.00165	0.0017	0.0017
LOD (ng•cm-2)	1.19	2.01	8.96

Reference:

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