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# On-site detection of phosgene agents by surface-enhanced Raman spectroscopy coupled with a chemical transformation approach

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Phosgene and its analogs are greatly harmful to the public health, environmental safety and homeland security as widely used industrial substances with extremely high toxicity. In order to rapidly evaluate the emergency risk caused by these chemicals, a new highly sensitive method based on surface-enhanced Raman spectroscopy (SERS) technique for measurement of phosgene agents was developed for the first time. Coupled with a chemical transformation approach, the highly toxic phosgene was conveniently converted to a SERS-sensitive probe, i.e. iodine ( $I_2$ ), with low toxicity or non-toxicity. The characteristic SERS peak in 459 cm<sup>-1</sup> was used for quantitation and was presumed as a formation of triiodide anion ( $I_3^-$ ), which was induced in an iodide ( $I^-$ )-aggregation Au NPs system. The total measurement can be completed in ~20 min with the limits of detection of ~60 µg/l (phosgene) and ~30 µg/l (diphosgene), respectively, on a portable Raman spectrometer. This work is the first report of SERS measurement on phosgene and diphosgene in a quantitative level. This method is expected to meet the requirements of on-site detection of phosgene agents, promote emergency responses and raise more opportunities for the portable SERS applications. Copyright © 2015 John Wiley & Sons, Ltd.

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Keywords: phosgene; SERS; chemical transformation approach; iodine; triiodide

# Introduction

Phosgene (carbonyl chloride, COCl<sub>2</sub>) is an important industrial substance employed in large quantities as a highly reactive halogenation and acylation agent in industry synthesis. Diphosgene (trichloromethyl chloroformate, ClCO<sub>2</sub>CCl<sub>3</sub>, C<sub>2</sub>O<sub>2</sub>Cl<sub>4</sub>) has a similar chemical property but is more suitable for main uses in the laboratory. These two industrial substances are ultrahigh toxic and have been classified as the choking chemical warfare agents several decades before.<sup>[1]</sup> Triphosgene (bis(trichloromethyl) carbonate, CO(OCCl<sub>3</sub>)<sub>2</sub>, C<sub>3</sub>O<sub>3</sub>Cl<sub>6</sub>), another compound related to phosgene, which is used as a substitute of phosgene due to its good stability and phosgene-alike reactivity,<sup>[2,3]</sup> also has a potential risk when it decomposes into phosgene under some certain conditions. The chemical structures of all three phosgene agents are shown in Fig. 1. Misuses or leakages of phosgene agents have attracted much attention from the industry and the whole society.<sup>[4]</sup> In 2004, a serious triphosgene leakage accident occurred in Fuzhou City (Fujian province, China). The injury symptoms appeared 4 h after the inhalation exposure, and then one death and 260 injuries were caused within 1 h. (Figure 1)

Phosgene agents are severe lung irritants, they can cause pulmonary edema, following asphyxia, and even death. The permissible exposure limit dose of phosgene is 0.1 mg/l, and the immediate danger to health and life limit dose is 2 mg/l.<sup>[5]</sup> In general, the human lung can be damaged with more than 30 mg/l phosgene exposure, and a fatal lung edema appeared with a dose higher than 300 mg/l.<sup>[6]</sup> A common lung injury hypothesis is believed that the acylation reaction rapidly occurred between phosgene and amino-, thiol- and hydroxyl- groups in the lung tissues, and the formed hydrolyzed products triggered the second damages, e.g. the acidosis induced by hydrochloric acids. Up to now, no antidote was discovered against the damage of phosgene. Therefore, on-site detection and rapid measurement of phosgene agents should arouse first and vital attention to ensure the prompt and accurate emergency response.

Over the past decades, several on-site detection methods for phosgene agents have been established, including mobile gas chromatography,<sup>[7,8]</sup> ion mobility spectrometry,<sup>[9,10]</sup> fluorescence spectroscopy, especially fluorescence resonance energy transfer (FRET),<sup>[3,11,12]</sup> and electrochemical methods.<sup>[13,14]</sup> Although these methods are simple, sensitive and easy-to-use, they still have some disadvantages or inconvenience. For example, ion mobility spectrometry and FRET methods sometimes offered false-positive responses.<sup>[2]</sup> The sensitivity and efficiency of FRET methods are often limited by the interference from the overlap between the donor emission and its acceptor.<sup>[3]</sup>

Surface-enhanced Raman spectroscopy can implement trace detection in aqueous solutions and provide the characteristic molecular vibration rotation fingerprint information. With a portable

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Figure 1. The chemical structures of all three phosgene agents.

Raman spectrometer, the surface-enhanced Raman spectroscopy (SERS) method can be evolved as a useful on-site analytical tool.<sup>[15,16]</sup> However, because phosgene can be easily decomposed in the aqueous solution and no strong Raman scattering formed due to its simple molecular structure even in the case of adsorption onto the surface of nanoparticles, it is impossible to directly measure phosgene itself. It may be one reason that there is no SERS report on phosgene so far. In order to address the previous issues and meet the needs of on-site measurement, here we developed a novel but indirect strategy for phosgene detection, in which we use potassium iodide (KI) to promote more Raman 'hot spots' and apply a chemical transformation to converse the highly toxic phosgene into the SERS-sensitive Raman probe (iodine, I2) with low toxicity or non-toxicity. The whole processes can be completed in ~20 min. The method is simple and practical, providing a new way for the detection of important threatened chemical substances that cannot be directly measured by SERS, and thus is promising for the practical countermeasures in potential public health threat, environmental pollution or terrorist attacks.

# **Experimental**

#### Material and instrument

Phosgene was made in-house under safe and strict protection. Diphosgene was obtained from the Research Institute of Chemical Defense (Beijing, China). Triphosgene was purchased from Alfa Aesar (MA, USA). I<sub>2</sub> was obtained from Beijing Chemical Reagent Company (Beijing, China) and was re-crystallized before use. Sodium iodide (Nal), potassium iodide (KI) and other chemicals were purchased from Sinopharm Chemical Reagent Co. Ltd. (Beijing, China). All chemicals were of analytical grade or better. Unless noted, all solutions were prepared in ultrapure water, which was generated from a Milli-Q A10 water purification system (Millipore, MA, USA).

The SERS spectra were collected on a portable Raman spectrometer (i-Raman, B&W TEK Inc., DE, USA) equipped with a video microscope sampling system (BAC151A, B&W TEK Inc.). The laser excitation wavelength was 785 nm, and the accumulation time of Raman spectra was 10 s with the averaged data for three scans. The laser power was set at 180 mW unless otherwise noted. Ultraviolet-visible absorption (UV–Vis) spectrometric measurements were performed on a Cary 300 double-beam UV–Vis spectrometer (Varian Inc., CA, USA). The zeta potential and particles diameter were obtained by a Zetasizer  $\mu$ V light scatter detector (Malvern Instrument Ltd., UK). Transmission electric microscope images were obtained from a Hitachi H-7650 instrument (Hitachi Technologies Co., Tokyo, Japan).

#### Preparation of phosgene

Because of the high toxicity of phosgene, all procedures must be performed in a ventilation cabinet. Triphosgene of 0.43 g was dissolved in hexane of 2.15 g in ice–salt bath, then a certain amount of dimethylformamide was slowly added until no bubble produced; the generated gas was phosgene, which was directly adsorbed in an acetone solution.

#### Preparation of gold nanoparticles-based SERS substrate

The gold nanoparticles (Au NPs) were synthesized according to a typical citrate reaction method.<sup>[15]</sup> An aliquot of 100 ml chloroauric acid solution at 100 mg/l was added to a 250 ml round-bottom flask, which connected with a reflux condensation. The solution was heated in oil bath with continuous stirring at 1500 r/min until stable reflux occurred. An aliquot of 850  $\mu$ l sodium citrate at 1% (w/v) ratio was then rapidly added into the chloroauric acid solution. After a few minutes, the color of solution was turned from dark red into violet color or blue. A continued heating and stirring was held for 40 min, then the solution was cooled to room temperature, and the Au NPs were generated. The shapes of Au NPs are round, with an average diameter from 50 to 52 nm, which is calculated from a published equation<sup>[16]</sup> according to the UV–Vis absorbance band at 530–532 nm and confirmed with transmission electric microscopy measurement.

To obtain the Au NPs-based SERS substrate, the Au NPs solution of 2 ml was centrifuged at 5000 r/min for 5 min, then re-dissolved in ultrapure water of 200  $\mu$ l; different kinds of potassium salt of 40  $\mu$ l at 50 mmol/l was then added as an aggregating agent, and the color of the whole solution was shown as middle violet. The aggregated Au NPs as a SERS substrate can be applied to the direct detection of converted product,  $I_2$ .

#### Chemical transformation of phosgene or diphosgene to iodine

For the measurement of phosgene and diphosgene, a chemical transformation approach was employed. According to the equations 1 and 2 in Fig. 2, phosgene and diphosgene can be quantitatively transformed to iodine according to a strict stoichiometric ratio at room temperature.

 $COCl_2 + 2 NaI = 2 NaCl + I_2 + CO$ (1)

$$C_2O_2Cl_4 + 4$$
 NaI = 4 NaCl + 2 I<sub>2</sub> + 2 CO (2)

Figure 2. The reaction equations of phosgene and diphosgene with sodium iodide.

To obtain a stock solution of  $I_2$  at 16 mg/l, phosgene of 16 mg/l or diphosgene of 8 mg/l was injected into an acetone solution of Nal with the concentration of 16 or 32 mg/l, respectively, and reacted at room temperature. It should be noted that the concentration of Nal can be set at slightly excess than theoretical concentration to ensure a complete chemical conversion. UV–Vis spectrometric monitoring results showed that both phosgene agents were turned into  $I_2$ with an ~100% yield in 15 min (Fig. S1). Later, a solution of  $I_2$  at 1.6 mg/l was prepared by direct dilution with acetone. Then, aliquot of 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0 and 8.0 µl of such a  $I_2$  solution was injected into 240 µl Au NPs, respectively, in which the concentrations of  $I_2$  were 8, 12, 16, 20, 24, 28, 32 and 64 µg/l, respectively. For a more dense solution of  $I_2$ , aliquot of 1.2, 1.4 and 2.0 µl of  $I_2$  stock solution at 16 mg/l was injected into 240 µl Au NPs, respectively, in which the concentrations of  $I_2$  were 96, 112 and 160 µg/l, respectively.

#### Determination of diphosgene in air

Different concentrations of diphosgene in air were tested as the real samples. First of all, the gaseous diphosgene of 5.6, 11.2 and  $16.8\,\mu$ I was injected into a flask full of air, respectively, then 10 ml Nal acetone solution was added into the flask to fully adsorb the

diluted diphosgene. The reaction was kept for 20 min at room temperature and was diluted for  $10^4$ -fold. Then, 1 µl diluted solution was added into 240 µl aggregated Au NPs for SERS measurement. The concentrations of I<sub>2</sub> were 12, 25 and 30 µg/l, respectively. Each sample was measured in triplicates.

# **Result and discussion**

#### Pretreatment of SERS sample and the chemical methods

Phosgene has a relatively simple structure, and the available Raman spectroscopy of phosgene can be only found as simulation data until now. Anantharishnan *et al.*<sup>[17]</sup> has reported that the computational simulation Raman shifts of phosgene are 302, 442, 573, 832 and 1803 cm<sup>-1</sup>, in which 573 and 1803 cm<sup>-1</sup> are the primary valence oscillations, 302 cm<sup>-1</sup> is a deformation oscillation, 832 cm<sup>-1</sup> is a valence type and 442 cm<sup>-1</sup> is one of the deformation oscillation at depolarized status. Direct and sensitive SERS measurement of phosgene is so difficult that no successful report can be followed. In our experiment, the SERS spectra of phosgene cannot be directly detected even at a 25 mg/l level in a portable Raman spectrometer with Au NPs (52 nm) or other common nanoparticle substrates.

To address the sensitivity issue, we proposed a chemical transformation approach inspired by the high reactivity of phosgene. At room temperature, phosgene or diphosgene can quantitatively react with Nal in a rapid, direct and specific manner, and then  $l_2$  was generated as the product. This reaction was rapid and can be completed in 15 min. The product  $l_2$  was thus measured as the specific analyte in SERS instead of phosgene agents. This chemical transformation approach avoids the phosgene hydroxylation, can be conveniently performed in aqueous or wet atmosphere and converts the highly toxic reactant to the low or non-toxic substances, which meets the on-site demand quite well.

#### Aggregation in the SERS measurement

Toward the practical and high-sensitivity aspect of SERS measurement, the structure of nanoparticles and thus induced 'hot spot' are always the important factors to be considered. 'Hot spots' is the gap region of a pair of strongly coupled nanoparticles,<sup>[18]</sup> and the highest Raman response of above 10<sup>6</sup> usually occurs at the inter-particle 'hot spot' in which the electromagnetic optical fields are highly concentrated.<sup>[19,20]</sup> The assembly of nanoparticles to aggregation is a very efficient way to obtain the 'hot spot', and various ways have been reported,<sup>[21]</sup> among them the inorganic salt induction way is the most convenient.<sup>[22,23]</sup> Here, ten kinds of potassium salts, including KF, KCl, KBr, KI, KNO<sub>3</sub>, KHCO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>, K<sub>2</sub>SO<sub>4</sub> and K<sub>3</sub>PO<sub>4</sub>, were used to induce the Au NPs particles aggregation.<sup>[24]</sup> The results of aggregation efficiency in Fig. 3 showed that KI was the best reagent to generate highest SERS response for 10 mg/l l<sub>2</sub> and the other three halogen (X) salts, KF, KCl and KBr, provided considerable enhancement. We assumed that X<sup>-</sup> could not only afford an one-atom-thick monolayer onto the surface of Au NPs and induced effective aggregation but also protect the existence of I<sub>2</sub> by forming triiodide ions  $(X_2I^-)$  anion<sup>[25]</sup> and thus tethered  $I_2$  into the 'hot spots' with an appearance of Raman sharp peak. The deduction was supported by further zeta potential and UV-Vis experiments. The salts of KNO3 and K2SO4 also offered comparable enhancement with KCl or KBr; the possible reason relies on the good affinity of Au–N or Au–S, which is benefit for the aggregation of Au NPs.<sup>[26]</sup> The salts of K<sub>2</sub>CO<sub>3</sub>, KHCO<sub>3</sub> and K<sub>3</sub>PO<sub>4</sub> only provided



**Figure 3.** The normalized surface-enhanced Raman spectroscopy (SERS) intensity of  $I_2$  (10 mg/l) on Au nanoparticles aggregated by different kind of potassium salt. All intensities were normalized to the intensity of KI-added case.

relatively low or no SERS enhancement effects. We then introduced KI as the aggregation agent for the SERS measurement of phosgene in the coming research (Scheme 1).

To further illustrate the enhancement effect of X<sup>-</sup> anion in this aggregation while  $I_2$  is coexisted, we have prepared nine kinds of Au NPs by simple chemical adsorption approaches and compared the UV–Vis absorption spectra, the diameters and zeta potentials of bare Au NPs, Au NPs@F<sup>-</sup>, Au NPs@CI<sup>-</sup>, Au NPs@Br<sup>-</sup>, Au NPs@I<sup>-</sup>, Au NPs@F<sup>-</sup>, Au NPs@I<sup>-</sup>, Au NPs@F<sup>-</sup>@I<sub>2</sub>, Au NPs@I<sup>-</sup>@I<sub>2</sub>, Au NPs@I<sup>-</sup>@I<sub>2</sub>, Au NPs@I<sup>-</sup>@I<sub>2</sub>, Au NPs@I<sup>-</sup>.

As shown in Fig. 4A, Au NPs exhibit a maximum Vis absorption peak at 532 nm. With the addition of X<sup>-</sup> anions, the intensity of this absorption peak is decreased. Furthermore, as shown in Fig. 4B, with the addition of iodine, a new peak of 352 nm appears in the formed Au NPs@l<sup>-</sup>@l<sub>2</sub> particle system. It is consistent with the  $I_3^-$  peak position previously reported,<sup>[27]</sup> which indicates that molecular polarization occurred as a product of the charge transition from I<sup>-</sup> anion to I<sub>2</sub>. It is also proved that in our chemical derivatization system of phosgene,  $I_3^-$  was actually generated. The peak of 261 nm in Fig. 4B is corresponding to  $I_2$  molecules.<sup>[27]</sup>

As shown in Table 1, when the  $X^-$  anions or  $I_2$  were mixed with the Au NPs solution, the hydrodynamic diameters of such nanoparticles have increased ~3-4 nm, while there is no obvious relationship between the thickness of the layer and the species of the anion or I<sub>2</sub>. When I<sub>2</sub> was further added into the Au NPs@X<sup>-</sup> solution, the corresponding hydrodynamic diameters were increased another 5 to 22 nm. This increase is so notable that some reunion could be formed, in which an aggregation state must be generated from the mono-disperse solution. When the Au NPs@X<sup>-</sup> were covered by a layer of X<sup>-</sup>, the highly negative charge of zeta potential from -29.0 to -36.6 mV were observed. When I<sub>2</sub> was further added, all the zeta potentials were increased at an extent of 10-13 mV. The Au NPs@l<sup>-</sup>@l<sub>2</sub> exhibit the largest zeta potential,  $-15.9 \,\text{mV}$ , which supports that the I<sup>-</sup> is tethered to the former added I<sub>2</sub>, and I<sub>3</sub><sup>-</sup> is thus formed as well as its zeta potential is increased a lot. The molecules of  $I_3^-$  in the 'hot spots' provide the largest response of SERS response, which leads to the successful detection of phosgene by an indirect method.

However, only in a suitable ratio that the KI can induce more SERS 'hot spots' to provide stronger SERS response. Our results



Scheme 1. The chemical transformation approach of phosgene agents in surface-enhanced Raman spectroscopy (SERS) measurement. NPs, nanoparticles.



Figure 4. The UV–Vis absorption spectra of Au NPs, Au NPs@F<sup>-</sup>, Au NPs@Cl<sup>-</sup>, Au NPs@Br<sup>-</sup> and Au NPs@I<sup>-</sup> (A) and the Au NPs@F<sup>-</sup> @l<sub>2</sub>, Au NPs@Cl<sup>-</sup> @l<sub>2</sub>, Au NPs@Br<sup>-</sup>@l<sub>2</sub>, Au NPs@I<sup>-</sup>@l<sub>2</sub>, Au NPs@I<sup>-</sup>@l<sub>2</sub>

Table 1. The hydrodynamic diameter, zeta potential and Vis absorption data of different Au NPs particles										
Kind of NPs	Au NPs	Au NPs @F	Au NPs @Cl <sup>-</sup>	Au NPs @Br <sup></sup>	Au NPs @I <sup></sup>	Au NPs @F <sup></sup> @l <sub>2</sub>	Au NPs @Cl <sup>-</sup> @l <sub>2</sub>	Au NPs @Br <sup>-</sup> @l <sub>2</sub>	Au NPs @I <sup></sup> @I <sub>2</sub>	Au NPs @I <sub>2</sub>
Hydrodynamic diameter (nm)	55.9	58.9	59.0	59.0	58.9	81.5	67.9	64.0	81.2	60.6
Potential (mV)	-35.7	-29.0	-36.0	-33.5	-36.6	-19.9	-16.4	-20.8	-15.9	-24.9
Ab of 532 nm	1.82	1.66	1.65	1.63	1.58	1.54	1.28	0.54	0.86	1.60
NPs, nanoparticle All data were trip	s. licated.									

showed that the best molecular ratio of salt to Au NPs was  $2 \times 10^7$ , i.e. when we kept the Au NPs at a concentration of 500 pmol/l, the correspondingly potassium salt was prepared at a concentration of 10 mmol/l. We further observed that the addition of excess ratio of salt destroyed the structures of the 'hot spots' and apparently produced a coagulation of the Au NPs, and then all the solution SERS signals deteriorated. The curve of SERS intensity *versus* the concentration of added KI is shown in Fig. S2.

The pH of the solution also influences the aggregation of nanoparticles. We investigated the pH value from 3.0 to 11.0 in the case of KI as the aggregation agent (data not shown). The results showed that the best aggregation occurred in the neutral pH.

### Characteristic Raman shift of 459 cm<sup>-1</sup>

To confirm that the Raman shift of  $459\,{\rm cm}^{-1}$  was exactly induced by  $I_2$ , but not by the other substances adsorbed onto the surfaces



Figure 5. The surface-enhanced Raman spectroscopy (SERS) spectra of spiked or formed I<sub>2</sub> at 1 mg/l (A) and the time-dependent curve (B).

of Au NPs, we investigated the SERS response of blanks, i.e. the blank substrate (the KI-aggregated Au NPs) and the blank sample (the acetone solution without I<sub>2</sub>). As shown in Fig. S3, the results showed that only a Raman shift of  $113 \,\mathrm{cm}^{-1}$  for Au–I bond appeared in the blank substrate, which was consistent with Xu's paper.<sup>[28]</sup> When the concentration of acetone is large enough, a characteristic Raman shift at 800 cm<sup>-1</sup> of acetone was observed in the blank sample. We also confirmed that the production of I<sub>2</sub> was the dominant factor contributed to the band of 459 cm<sup>-1</sup> by standard spiking method. The addition of pure standard I<sub>2</sub> of 1 mg/l into the KI-aggregated Au NPs also induce the same 459 cm<sup>-1</sup> shift, as shown in Fig. 5A. This consistency proves that the Raman shift of 459 cm<sup>-1</sup> is indeed the shift of the product I<sub>3</sub><sup>-</sup> and can be used as the characteristic shift in our chemical transformation method.

A time-dependent tendency occurred toward the  $I_2$  product either obtained from the chemical transformation method or as a standard added into the KI-aggregated Au NPs. The SERS intensity is gradually increased with the elapsed time, reaches the maximum at 5 min and can be kept at least 1 h without obvious decrease (Fig. 5B). Thus, all samples were measured in 5 min after the addition of the analyte. Because  $I_2$  is not so stable due to its medium reactivity, it is believed that the formation of  $I_3^-$  is largely helpful to maintain the stability of SERS signal in the case of KI-aggregated Au NPs. This continued signal is very convenient for us to perform the on-site measurement.

The Raman shifts of  $I_3^{-}$  in aqueous solution are reported at below 150 cm<sup>-1,[29]</sup> However, as noted by Ref. [30], the kind of solvent affected the Raman shift of triiodide anions a lot. We compared three kinds of organic solvent–water mixed systems with aqueous solution and found that the Raman peak of 459 cm<sup>-1</sup> appear in three organic solvent–water mixed systems but disappear in aqueous solution, in which the acetone–water mixed system contributes the largest intensity (Fig. 6). Here, we suppose that the 459 cm<sup>-1</sup> in our SERS case is belonging to the red shift of which commonly observed below 150 cm<sup>-1</sup> in aqueous solution in Raman spectroscopy, and the large red shift might due to the ultra stability of triiodide in mixed acetone–water system and the surface-enhanced Raman shift effect.

# Quantitative measurement of phosgene and diphosgene, and the reaction behaviors of three kinds of phosgene agents

The SERS band of  $I_3^-$  has a distinct single peak at 459 cm<sup>-1</sup>, which is more conductive for semi-determination or quantitative



**Figure 6.** The surface-enhanced Raman spectroscopy spectra  $I_2$  at 5  $\mu$ g/l in three kinds of organic solvent-water mixed systems and in aqueous solution. Dimethyl sulfoxide (DMSO).



**Figure 7.** The surface-enhanced Raman spectroscopy spectra at 459 cm<sup>-1</sup> versus the concentrations of  $l_2$  from 8 to 160  $\mu$ g/l (A); the inserted figure (B) shows the linear curve of  $l_2$  from 8 to 32  $\mu$ g/l.

determination in SERS. As shown in Fig. 7, it has a good SERS response from 8 to  $160 \mu g/l l_2$ , with the linearity from 8 to  $32 \mu g/l (r^2 = 0.973)$ , and a limit of detection (LOD) is as low as ~3  $\mu g/l$ . When the concentration of  $l_2$  was beyond  $160 \mu g/l$ , its SERS intensity reached a platform, which means that the  $l_2$  was saturated at



Figure 8. The UV–Vis time-dependent absorbance curves at 365 nm (A) and the time-dependent surface-enhanced Raman spectroscopy intensity (B) of  $I_3^-$  product, which was generated by phosgene, diphosgene and partially decomposed triphosgene.

the surfaces of the KI-aggregated Au NPs. Toward diphosgene and phosgene in our chemical transformation method, the LOD were 30 and  $60 \mu g/l$ , respectively.

In our experiment, the LOD of I<sub>2</sub> was ~3 µg/l, which was much lower than the results of UV–Vis spectrometry,<sup>[31]</sup> starch colorization<sup>[32]</sup> and FRET<sup>[33]</sup> as their LODs were at milligrams per liter level. This method affords a great potential to achieve more sensitivity. Another aspect should be noted, phosgene agents are prone to be hydrolyzed in aqueous solution, but through this chemical transformation approach in a mixed water–acetone solution, the hydroxylation could be ignored.

In this chemical transformation approach, phosgene and diphosgene can be easily reacted with Nal in acetone solution at room temperature, and the products include I<sub>2</sub>, sodium chloride (NaCl) and carbon monoxide (CO).<sup>[34]</sup> Because triphosgene can be readily decomposed into phosgene, we expect that triphosgene also can be monitored by this method. Considering that the same concentration of  $I_2$  product at 50 mg/l, phospene of 50 mg/l and diphosgene of 25 mg/l were used in this chemical transformation method according to the stoichiometric ratio; we also prepared triphosgene of 17 mg/l based on that one triphosgene molecule can be totally decomposed to three phosgene in the most ideal condition. The UV-Vis absorbance data and SERS intensity of the produced  $I_3^-$  over time are shown in Fig. 8. Triphosgene with the lowest reaction rate in comparison with phosgene and diphosgene were also detected using this chemical transformation approach; the main reason is due to its partial decomposition fate.

#### Determination of phosgene and diphosgene in air sample

To validate our method, we also constructed the contaminated air samples by mixing the gaseous diphosgene into the air as an example. We obtained the recovery from 85% to 109% for diphosgene (Table S1), indicating that our method is very convenient and reliable for on-site measurement of phosgene or diphosgene.

# Conclusion

We firstly developed a simple, sensitive and rapid chemical transformation method for the quantitative measurement of phosgene and diphosgene using SERS technique. The iodide salt was discovered as the efficient aggregation agent to achieve high sensitivity for detection of the product  $I_2$ . Phosgene and diphosgene, even triphosgene, can be indirectly measured with LODs as low as dozens of micrograms per liter. This chemical transformation is proved to be quite feasible in the determination of contaminated air samples. We believe that this SERS method has potential to be employed in the emergency responses toward public health, environmental safety and homeland security.

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# **Supporting information**

Additional supporting information may be found in the online version of this article at the publisher's web site.