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Surface-enhanced Raman spectroscopy detection of polybrominated diphenylethers using a portable Raman spectrometer

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ABSTRACT

Polybrominated diphenylethers (PBDEs), one of the most common brominated flame retardants, are toxic and persistent, generally detected by the chromatographic method. In this work, qualitative and quantitative detection of PBDEs were explored based on surface-enhanced Raman spectroscopy (SERS) technique using a portable Raman spectrometer. Alkanethiol modified silver nanoparticle aggregates were used as the substrate and PBDEs could be pre-concentrated close to the substrate surface through their hydrophobic interactions with alkanethiol. The effect of alkanethiols with different chain length on the SERS detection of PBDEs was evaluated. It was shown that 1-hexanethiol (HT) modified substrate has higher sensitivity, good stability and reusability. Qualitative and quantitative SERS detection of PBDEs in real sea water was accomplished, with the measured detection limits at 1.2×10^2 μg L^{-1}. These results illustrate SERS could be used as an effective method for the detection of PBDEs.

1. Introduction

Polybrominated diphenylethers (PBDEs) are one of the most common brominated flame retardants (BFRs), which have been widely found in various consumer products [1]. PBDEs are composed of two phenyl rings linked by an oxygen atom with variable hydrogen to bromine substitutions, and there are theoretically 209 possible congeners. PBDEs are lipophilic (log Kow 5.0–8.3), resistant to chemical and biological metabolism and persist in the environment [2]. As one of the most widely used BFRs, tens of thousands of tons of PBDEs are manufactured every year and the levels of PBDEs in the environment show a marked increase [3]. PBDEs are detected in most environmental matrixes, such as water, soil, air, sediments and breast milk [4–10]. In addition, PBDEs might be converted to high toxic PBDEs byproducts, such as polybrominated dibenzofurans (PBDF) and polybrominated dibenzodioxins (PBDD) by photochemical degradation or pyrolysis, which are also ubiquitous in environment [11]. Recently laboratory studies suggest that PBDEs are posing potential health risks, such as hormone disruptors, adverse neurobehavioral toxics and reproductive/developmental effects [12,13]. PentaBDEs and octaBDEs have been listed recently as persistent organic pollutants (POPs) in the Stockholm Convention due to their persistent and bioaccumulative characteristics [14]. It is crucial to monitor PBDEs in the environment. Gas chromatography (GC) coupled with electron capture detector (ECD) or mass spectrometry (MS) and high-performance liquid chromatography (HPLC) coupled with UV or MS have been usually used for the detection of PBDEs [15,16]. However, GC analysis of PBDEs is difficult because of the thermal degradation problems [15] and HPLC analysis may suffer from adequate resolving power for PBDE congeners [16]. Moreover, Pre-concentration of the target compounds is usually needed prior to chromatographic analysis, which is complex and time-consuming. To evaluate the movement, fate and global distribution of PBDEs, it is quite important to develop a convenient, rapid and sensitive analytical method.

As a non-destructive technique, Raman spectroscopy can provide rich information about molecular composition and structure. However, the universal application of Raman spectroscopy as a basic analytical tool is restricted by the low intensity of normal Raman signals [17]. Surface-enhanced Raman spectroscopy (SERS) is a commonly used analytical technique, which could amplify Raman signals when the Raman-active molecules are close to the substrate surface [18,19]. SERS has been widely used in chemical, environmental and biological related sensing due to its high sensitivity and good selectivity [20,21]. Large SERS signals could be obtained when the analytes are very close to the substrate surface. However, many analytes, such as PBDEs and polychlorinated biphenyls (PCBs), show weak affinity to the substrate surface, which makes their direct detection by SERS difficult. Fortunately, the problem could be addressed by modifying the substrate with proper functional entities or self-assembled monolayers (SAMs) [22,23]. Hence, the analytes could be adsorbed close to the substrate surface through their interactions with the surface modifier of the substrate [24,25].

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In this work, qualitative and quantitative detection of PBDEs were performed based on SERS using a portable Raman spectrometer. Alkanethiol modified silver nanoparticle aggregates were used as the substrate and the SERS sensitivity of different alkanethiols modified substrate were compared. The uniformity, stability and reusability of alkanethiol modified substrate were evaluated. Qualitative and quantitative detection of PBDEs in real sea water were realized by SERS. Additionally, the Raman spectra calculated using the Gaussian 03 code yield results that match the experimental observations.

2. Experimental

2.1. Materials

Silver nitrate, PVP-K30, sodium chloride (NaCl) and copper foils (Cu, 10 cm × 10 cm in size, 0.1 mm in thickness, 99.99%) were purchased from Sinopharm Chemical Reagent Co.,Ltd. 1-Hexanethiol ($CH_3(CH_2)_5SH$) (HT), 1-dodecanethiol ($CH_3(CH_2)_{11}SH$) (DT), 1-octadecanethiol ($CH_3(CH_2)_{17}SH$) (ODT) and tin dichloride ($SnCl_2 \cdot 2H_2O$) were obtained from Aladdin Chemistry Co., Ltd. 4,4′-Dibromodiphenyl ether (BDE-15) was purchased from Aldrich. Ultrapure water (18.2 MΩ cm) was used throughout the experiment. The real sea water was obtained from Yellow sea and filtered through a 0.22 μm syringe filter before use.

2.2. SERS substrate fabrication and incubation procedure

The substrate with high enhancement factor is quite important for the SERS detection, and noble metal nanostructure is the commonly used substrate materials. Silver nanoparticle aggregates on copper foil prepared by simply galvanic displacement reaction were found to be high SERS sensitive, which was selected as the substrate in this work. The procedure for the preparation of the substrate was described in our previous work [26].

The prepared substrate was immersed in ethanol solution containing 1 mM alkanethiol for 12 h to prepare alkanethiol modified substrate [27,28]. Prior to incubation in PBDEs solution, the substrate was rinsed with absolute ethanol and allowed to air dry. Alkanethiol modified substrate was immersed in the analyte solution for 3 h, then Raman signals were collected.

The analyte solution was prepared by dissolving PBDEs in ethanol, and then diluted to a desired concentration with ultrapure water wherein it is more soluble. PBDEs solutions in real sea water were also obtained.

2.3. SERS detection

All the Raman measurements were performed with an Ocean Optics QE65000 spectrometer. The excitation wavelength was 785 nm, the laser power was 440 mw, and the integration time was 1 s for the SERS spectra unless the special note.

3. Results and discussion

3.1. Functionalization of the substrate with alkanethiol

SERS signals could be obtained when Raman-active molecules are close (viz., 0–4 nm) to the surface of noble metal (mainly refer to gold and silver) nanostructures [29,30]. However, PBDEs show weak affinity to noble metal surface, which makes their direct detection by SERS difficult. Alkanethiols are selected as the surface modifier, as they are easy to form densely packed self-assembled monolayers (SAMs) on the metal surface by spontaneous chemisorption of the S to metal [27,28]. PBDEs could be concentrated close to the substrate surface through their hydrophobic interaction with alkanethiols, which would make their detection by SERS possible. It has been reported that the SERS sensitivity is largely influenced by the chain length of alkanethiols [31]. Alkanethiols with different chain length (C6, C12 and C18) were used in this work. Functionalization of the substrate with alkantehiols was confirmed with SERS spectra and their corresponding Raman spectra of the alkanethiols were used for comparison in this work. The Raman bands in the SERS spectra are comparable to that in Raman spectra (data not shown), suggesting alkanethiols had adsorbed on the substrate surface.

3.2. Detection of PBDEs with three different alkanethiols modified substrate

To assess whether PBDEs could adsorb onto the three different alkanethiols modified substrates, the substrates were immersed in the analyte solution and their SERS spectra were recorded. BDE-15 was selected as the probe to investigate the SERS enhancement effect of different alkanethiols modified substrate. Fig. 1 shows the SERS spectra of BDE-15 on three different alkanethiols modified substrate and the Raman spectrum of its powder for comparison. As shown in Fig. 1A, the characteristic Raman bands of BDE-15 powder appear at 1586, 1196, 1164, 1076, 780, 711 and 651 cm^{-1}. Fig. 1B–D all have the characteristic Raman peaks of BDE-15, which indicates that all the three different substrates could adsorb BDE-15.

To evaluate the sensitivity of alkanethiol modified substrate to PBDEs, three different alkanethiols modified substrate were exposed to various concentrations of BDE-15 solution and recorded their corresponding SERS spectra. Fig. S1 shows the SERS spectra of BDE-15 with increasing concentrations based on HT, DT and ODT modified substrate. It could be seen that the Raman intensity of BDE-15 increases gradually with the increasing of analyte concentration. The enhancement order to BDE-15 is HT>DT>ODT-modified substrate, which indicated the decrease in the Raman signals as the chain length increased. This result is in agreement with the previous reports about the SERS detection of aromatic compounds based on different alkanethiols modified substrate [31]. HT-modified substrate was selected for the following work due to its higher SERS sensitivity.

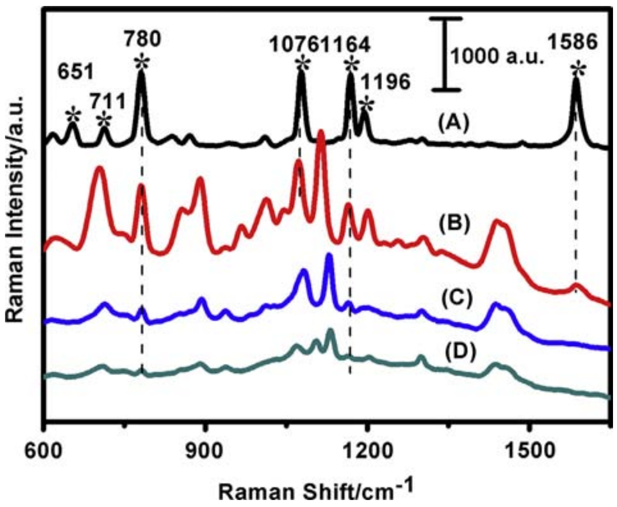

Fig. 1. Raman spectrum of BDE-15 powder (A), SERS spectra of BDE-15 on (B) HT, (C) DT and (D) ODT modified substrate.

3.3. Stability and reproducibility of HT modified substrate

It is known that stable SERS signals are quite important to obtain accurate, quantitative analytical results. However, the SERS response could be influenced by temperature and the laser radiation [32–34]. Hence, stable substrate seems crucial to SERS analytical technique. Our previous work has proved that the silver nanostructures on the copper foil were quite stable [26]. Silver nanoparticle aggregates on copper foil were selected as the substrate in this work. Our previous work has proved that the HT-modified substrate has good uniformity and temporal stability [26]. Here, the long-term stability of the substrate was evaluated by comparing the SERS spectra of BDE-15 on the freshly prepared substrate and the substrate immersed in the BDE-15 solution for several days. As shown in Fig. S2, neither the overall shape nor the bands intensity of the SERS spctrum has obvious change after the substrate was immersed in the solution for 5 days, which indicated the long-term stability of the substrate is quite good.

Other than the stability and uniformity, the reusability is another important parameter for the SERS substrate [35,36]. The reusability of the substrate was investigated through examining the partition/departition process of PBDEs on HT modified substrate. HT modified substrate was immersed in the solution of BDE-15 and methyl alcohol in a cyclic fashion and their corresponding SERS spectra were recorded (Fig. S3). After the substrate was immersed in the BDE-15 solution for 2 h, the characteristic Raman peaks of BDE-15 at 780, 1076 and 1164 cm^{-1} appeared on the spectra, which illustrates the analyte had partitioned into the SAMs. As shown in Fig. S3B, D, F, H and J, when the substrate was immersed in methyl alcohol for 1 min, the characteristic Raman peaks of BDE-15 disappeared, which indicated that BDE-15 had been eluted from the SAMs. Compared Fig. S3I with Fig. S3A, it could be illustrated that HT modified substrate still has good adsorption effect to BDE-15 after five cycles, which indicates the substrate has good reusability. Hence, it is reasonable to select HT modified substrate for the following experiment.

3.4. Detection of PBDEs in real sea water

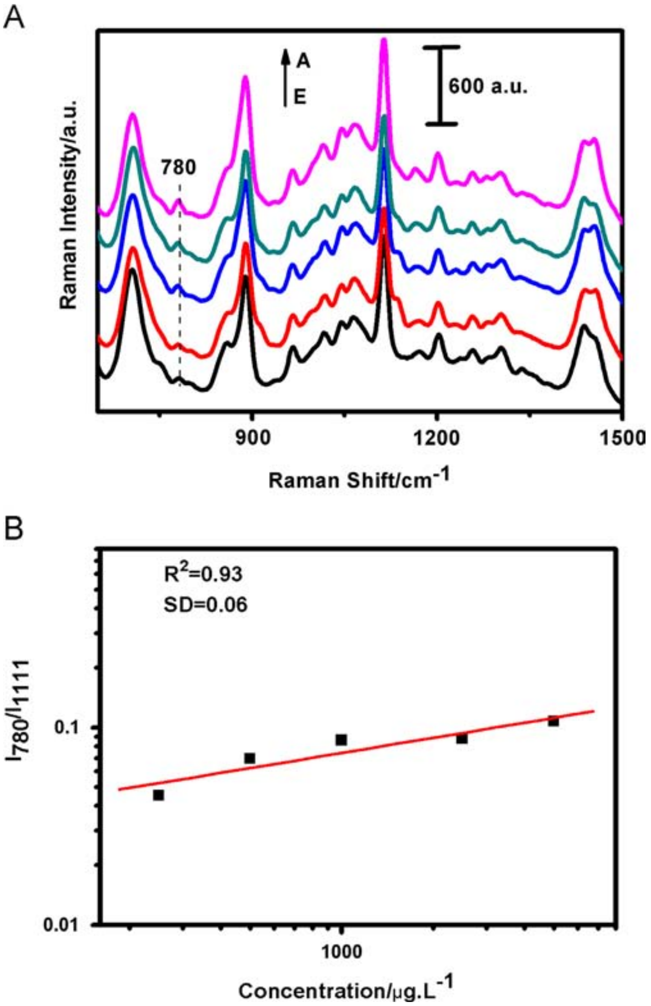

Fig. 2. (A) SERS spectra and (B) log–log plot for BDE-15 in the real sea water based on HT modified substrate.

In order to investigate whether SERS could detect PBDEs in the real-world water, the probe (BDE-15) was dissolved in real sea water. Prior to recording the SERS spectra, the HT modified substrate was immersed in PBDEs solution for 3 h. The sensitivity of HT modified substrate to PBDEs in the real sea water system was tested by immersing the substrate into various concentrations of BDE-15 solution. Fig. 2A shows the SERS spectra of the substrate after being immersed into different concentrations of the analyte for 3 h. The intensity of the SERS peak at 780 cm^{-1} increases with increasing the concentration of BDE-15 over the concentration range of 2.5×10^2 μg L^{-1} to 5.0×10^3 μg L^{-1}. The initial Raman intensity of both BDE-15 and HT in the real sea water was lower than that in the ultra-pure water solution, which was ascribed to the interference by the various salts or organic species in the real sea water. Quantitative analysis of BDE-15 in real sea water was also conducted. As the concentration of HT was a fixed value, the intensity of their Raman band could be considered as constant. The most obvious Raman band of HT at 1111 cm^{-1} was selected as the reference for the spectrum normalization. The normalized intensity of BDE-15 at 780 cm^{-1} was used to study the SERS sensitivity of HT-modified substrate as the function of BDE-15 concentrations. The log–log plot of the normalized intensity at 780 cm^{-1} to the analyte concentration exhibits a good linear relationship as shown in Fig. 2B. The linear regression equation is $y=-2.13+0.34x$ (where x is logarithm of the BDE-15 concentration and y is logarithm of the normalized SERS intensity of Raman peak at 780 cm^{-1}) with the correlation coefficient of 0.93. The detection limit of BDE-15 was 1.2×10^2 μg L^{-1} (3 times the standard deviation above the blank). The precision of the method was evaluated and the relative standard deviation (RSD) of the data was 4.8% for a concentration of 1.0×10^3 μg L^{-1} BDE-15 ($n=3$).

As far as we know, this is the first example to detect PBDEs employing SERS technique. By modifying the substrate with alkanethiol, PBDEs could be concentrated close to the substrate surface, which makes their detection by SERS possible. Application of the SERS technique in the detection of PBDEs has several unique advantages. Firstly, this technique is quite simple [37]. Secondly, the SERS technique is fast, using only several seconds to acquire one spectrum [38]. Thirdly, due to its fingerprint characteristics, SERS could perform well in the mixed sample, without the pre-separation [39].

3.5. Theoretical calculate the Raman spectra of PBDEs congeners

To gain a better understanding of these features, Raman spectra of PBDEs were calculated using Gaussian 03 program package (B3LYP/6-311G**) [40–42]. Their molecular structures were optimized by density functional theory (DFT). In order to determine whether the calculated results are accurate, the calculated Raman spectrum of BDE-15 was compared with the experimental result. It could be seen in Fig. 3 that the calculated Raman bands are in good agreement with the experimental data, which indicates the calculated results are accurate. The vibrational modes of each

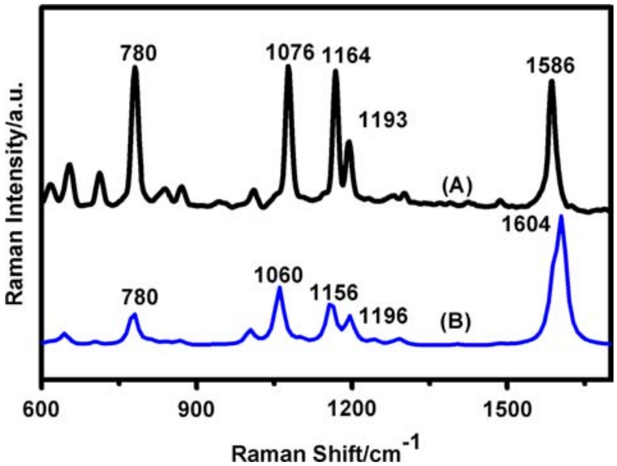

Fig. 3. (A) Experimental and (B) calculated Raman spectra of BDE-15.

Raman peak could be analyzed using Gauss View 5.0 software, which may help us to better understanding the assignment of the experimental results.

4. Conclusions

The above results reveal that it is possible to realize the detection of PBDEs based on SERS technique. HT modified substrate has good stability and reusability, which shows higher sensitivity to PBDEs than that of DT or ODT modified substrate. Qualitative detection of PBDEs dissolved in ultra-pure water and real sea water were realized. Quantitative detection of PBDEs was also realized as the log–log plot of the normalized Raman intensity of PBDEs to its concentration exhibits a good linear relationship. This method achieved quantitative detection of BDE-15 in real sea water ranging from $2.5 \times 10^2\ \mu g\ L^{-1}$ to $5.0 \times 10^3\ \mu g\ L^{-1}$ and provided a detection limit of $1.2 \times 10^2\ \mu g\ L^{-1}$. Calculations were further carried out to obtain the theoretical Raman spectra of PBDEs, which agreed well with the experimental data. These results show SERS could be used as a routine analytical technique to monitor the PBDEs.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2013.04.056.

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