Highly sensitive sensing and quantitative detection of sulfate ion with a SERS chip-based on boric acid’s Lewis effect

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Abstract
Based on the Lewis acid’s coordination principle, a surface-enhanced Raman scattering (SERS) chip strategy had been developed for the ultrasensitive quantitation of $\text{SO}_4^{2-}$. Through the immobilization of silver nanoparticles (Ag NPs) and the construction of the boric acid-based sensing unit, the chip system displayed outstanding merits on the direct sensing of $\text{SO}_4^{2-}$, e.g., simple operation, ultra-high sensitivity, reproducibility, excellent selectivity and specificity. Moreover, an accurate evaluation was obtained by ratiometric calculations on characteristic peaks (1382 and 1070 cm$^{-1}$) for quantitative detection of $\text{SO}_4^{2-}$. The detection limit was down to 10 nM. Tap water, beer, and mineral water samples were tested, and high recoveries were achieved (97.12–110.12%). Besides, such SERS chip also displayed strong applicability for the evaluation of $\text{SO}_3^{2-}$. Therefore, this SERS chip provided a promising idea for the quantification of trace amounts of $\text{SO}_4^{2-}$ and $\text{SO}_3^{2-}$ in the fields of food safety and environmental monitoring.

Keywords SERS · Sulfate anion · 4-Mercaptoboric acid (4-MPBA) · AgNPs chip · Lewis acid–base theory

Introduction
Anions, as indispensable components in living organisms, play crucial roles in several physiological and chemical activities. However, the insufficiency and overdose of anions could also induce serious metabolic and/or toxicological diseases [1]. Among the various anions, sulfate anion ($\text{SO}_4^{2-}$) plays an irreplaceable role during the organismal metabolisms and biosynthesis [2]. It is well known that the sulfate anion is closely related to the formation of synovial membranes in joints and mucin proteins. Moreover, it had been confirmed that low levels of sulfate in plasma may lead to rheumatoid arthritis and irritable bowel diseases [3]. Notwithstanding, the ingestion of high-concentration sulphate would cause serious physiological pathema such as skin and eyes irritation diarrhea, dehydration, gastrointestinal disorders, and even respiratory paralysis [4]. Therefore, due to the increasing industrial emissions and metabolic accumulation in organisms, it is essential and profound to accurately evaluate the content of $\text{SO}_4^{2-}$ ion in our environment and food chains.

Unfortunately, up to now, the conventional methods for the detection of $\text{SO}_4^{2-}$ ion in the world are still based on the turbidimetric test, gravimetric method and EDTA titration. Such conventional techniques, undoubtedly, are readily operated. However, the low sensitivity, insufficient selectivity, anti-interference abilities, and operator dependence highly constrain its accurate performance [5]. To solve these issues, recently, various strategies based on advanced facilities, e.g., electrophoresis [6], ion-selective electrodes [5], ion chromatography [7], and atomic emission spectrometry [8, 9], had been established for the detection of $\text{SO}_4^{2-}$ ion. Such alternative techniques displayed various advantages on the sensing of $\text{SO}_4^{2-}$ ion during tests in the laboratory, e.g., excellent sensitivity and solid repeatability. However, it should be stated that the professional and skilled operations on
expensive devices must be employed if one wants to obtain a good performance in a low concentration of sulfates with these methods. To fill in the gap on the sensitive detection of SO$_4^{2-}$ ion, the ultra-sensitive, simple, rapid response, and handy operation techniques are urgently needed.

Surface-enhanced Raman scattering (SERS) spectroscopy as an ultra-sensitive molecular sensing technique [9, 10] had been widely utilized in various fields, e.g., chemistry [11], biomedicine [12], environmental monitoring [13], and food science [14, 15], due to its instant information acquisition on multiple molecules. Being different from organic molecules, most of inorganic ions cannot directly generate Raman signals, therefore, specific probes must be designed for ion detection in Raman spectroscopy [16, 17]. Also, the development of specific sensors for identification and detection on various ions is one of the current hot-topics in SERS technology. For example, through modifying the probe molecules grafted on gold or silver nanoparticles (Au/Ag NPs), numerous researchers had achieved the quantification of target ions, such as Hg$^{2+}$ and Zn$^{2+}$ ions [18]. 2,5-Dimercapto-1,3,4-thiadiazole (DMcT) [19] and N,N-bis(2-hydroxybenzylidene)-4-aminophenyl disulfide (HBA) [20], which have high binding constants with Hg$^{2+}$ and Zn$^{2+}$ ions, respectively, were modified to the Ag nanoparticles as recognition receptors. The formation of strong Hg–N, Zn–N, and Zn–O coordination bonds realized the recognition of Hg$^{2+}$ and Zn$^{2+}$ ions. Yet, in general, different with the stable cations, a higher complementarity is required for probes to be selective for target anions because of wide range of geometries and the more diffuse nature of larger size anions. Besides, the sulfate anions usually exist in different charge states, following the pH variance of an aqueous solution [21]. Moreover, the high hydration energies (~1080 kJ/mol) and hydrophilicity of SO$_4^{2-}$ ion also severely hinder the performance of sensitive detection of SO$_4^{2-}$ ion with Raman spectroscopy [22]. According to theoretical calculations, strong hydrogen bonds had been confirmed between oxygen atoms of SO$_4^{2-}$ and H$_2$O molecules. Meanwhile, one sulfate ion could construct up to 12 hydrogen bonds with H$_2$O molecules [23].

Due to the multivariate charge states and high hydration energy, the development of specific sensing probes with high selectivity and affinity on SO$_4^{2-}$ ion is being an exciting challenge in the analytical fields of environment and food science. For example, according to the potential of multiple hydrogen bonds construction, thioureas [24], squaramide [25], pyroles [26], imidazolium [3], and indoles [27] had been employed as hydrogen-bond donating units for SO$_4^{2-}$ sensing in aqueous solution. Moreover, to improve the sulfate binding affinity, a double pyrroles probe, i.e., bipyrrrole strapped calix [4] pyrroles, was synthesized and developed as a sulfate receptor [26]. Unfortunately, the low synthesis yield and relatively weak selectivity largely limited such hydrogen donated strategies. Recently, to achieve a strong and selective binding, Qin et al. [3] proposed a guidance for improving the selectivity of SO$_4^{2-}$ ion sensing based on a series of macrocyclic squaramide-containing receptors construction and corresponding DFT calculations. That is, sensing receptors for target ions should be designed to match their conformations, including the size and shape. Although these pathbreaking achievements have indicated new directions for ion sensing, the study on direct quantification of SO$_4^{2-}$ ion with SERS has been still blank so far due to its tetrahedral structure and divalent electricity.

Herein, a novel chip strategy for quantitative sensing trace amounts of SO$_4^{2-}$ ion has been developed based on the Lewis’ effect and SERS technique. As illustrated in Fig. 1, cheap and easily available 4-mercaptoboric acid (4-MPBA) was employed as a sensing receptor in our protocol. In view of the short chain of 4-MPBA and the absolute boric acid sensing unit, which is electron-deficient and could specifically identify polyols and Lewis bases [28, 29], plasma bases were readily constructed for sensitively indicating the SO$_4^{2-}$ ion. Based on such chip strategy, the SO$_4^{2-}$ ion could be easily monitored with good reproducibility even though its concentration was down to 10 nM. Meanwhile, most of the interfering ions could not affect the specific selection during the chip sensing. Importantly, our SERS chip strategy provided an over 4 orders of magnitude lower than that prescribed by WHO for the content of SO$_4^{2-}$ ion in tap water under acceptable recoveries, and it also maintains great potential on sensing of SO$_4^{2-}$ ion. In the present study, the construction and sensing mechanism for our chip strategy shall be systematically introduced in detail.

**Experimental section**

**Materials and reagents**

Sodium citrate (purity > 98%) and 3-aminopropyltriethoxysilane (APTES, purity > 98%) were purchased from Sigma-Aldrich. 4-mercaptoboronic Acid (4-MPBA, purity > 90%) was obtained by Aladdin Chemistry Co. Ltd. (Shanghai, China). All other chemicals with AR grade were supplied by Sinopharm Chemical Reagent Co. (Shanghai, China).

**Synthesis of silver nanoparticles (Ag NPs)**

Citrate-stabilized Ag NPs were synthesized following the conventional sodium citrate reduction strategy [30]. That is, the sodium citrate solution (1%, 2 mL) was added into a boiling AgNO$_3$ aqueous (1 mM, 100 mL) under vigorous magnetic stirring for 1 h. Subsequently, the color of the solution turned to gray, the mixture was cooled down to
room temperature and finally was stored at 4 °C as a stock solution.

**Preparation of 4-MPBA-functionalized monolayer Ag NPs chip**

Ultra-hydrophilic glass coverslips were first prepared following our previous proposed protocol [31]. Subsequently, the APTES molecules were chemically grafted onto the glass surface under the vapor phase. The detailed operation of APTES grafting could be found in our previous reports [31]. After the modification of APTES, a ten-fold condensed Ag NPs colloid was deposited directly on the glass overnight to achieve monolayer Ag NPs. Soake monolayer patterned Ag NPs chips in a 4-MPBA ethanol solution (1 mM) at room temperature, ca. 25 °C, for overnight or long-term store as stock. Developed 4-MPBA functionalized chips should be thoroughly rinsed with ethanol and naturally dried at room temperature before operating the evaluation.

**Characterizations of NPs functionalized chips**

UV–vis spectra were recorded on an Avaspec-2048 UV–vis spectrophotometer (Shimadzu, Japan). Transmission electron microscopy (TEM) images were acquired through operating a JEOL JEM-2100 transmission electron microscope with an acceleration voltage of 200 kV. Scanning electron microscopy (SEM) images of the chips were obtained with an ultra-high resolution SEM system (SU-8230, Jeol Japan). Raman spectra were measured on a micro-Raman system equipped with an excitation laser of 532 nm (Dxr2xi, Thermo Fisher).

**SERS chip evaluation and detection**

Before the measurements of SERS spectra, 4-MPBA modified glass chips were immersed in the 1.5 mL solution with different concentrations of the $\text{SO}_4^{2-}$ ion, respectively. Different concentrations of $\text{SO}_4^{2-}$ ion were obtained via serial dilution of standard $\text{K}_2\text{SO}_4$ solution ($1.0 \times 10^{-2}$ M). For Raman spectra measurements, the laser power was set at 2.0 mW, and the exposure time for each measurement was 0.01 s with a ten-fold accumulation. In this study, all baseline-corrected SERS spectra were normalized using the band of 4-MPBA at 1070 cm$^{-1}$.

**Real sample analysis**

Tap water ($\text{pH} = \text{ca.} 7$) was directly collected from our laboratory. Afterward, the sulfate was added into the samples and obtain different concentrations of $\text{SO}_4^{2-}$ ion ranging from $1.0 \times 10^{-4}$ to $1.0 \times 10^{-6}$ M. To quantitatively evaluate the performance of the as-prepared SERS chip, the chips were soaked in water samples (ca. 1.5 mL) for 10 min, and then, the SERS spectra were collected under the same parameters as the chip evaluation. Mineral water and beer samples were purchased from a supermarket in Wuxi. The samples were processed with reference to the preparation process of tap water. For Beer, it was diluted onefold with water, and sonicated for 30 min. The supernatant was collected after centrifugation, and was purified using an RP column, the filtrate was collected for Raman analysis.
Results and discussion

Mechanism for sensing the $\text{SO}_4^{2-}$ ion with 4-MPBA functionalized SERS chip

It is well known that boric acid is a typical Lewis acid, and the vacant $p$-orbital on boron can accept a pair of electrons for the formation of a coordination bond. Moreover, the hybridization state of the boron atom could change from $\text{sp}^2$ to $\text{sp}^3$ when a negative charge was introduced [28, 32]. According to such self-correction action, currently, several colorimetric and fluorescent derivatives based on 4-MPBA had been developed for the detection of fluoride ion ($\text{F}^-$) [33]. Inspired from boron-fluorination reaction and deliberate inference, as shown in Fig. 2, we found that when the 4-MPBA molecule was exposed to $\text{SO}_4^{2-}$ ion, the group of hydroxyl oxygen in $\text{SO}_4^{2-}$ ion could provide a pair of unshared electrons to the boric acid group via a dehydration reaction, and the boron atom at the center of 4-MPBA changed from a trigonal planar moiety of $\text{sp}^2$-hybridization to the $\text{sp}^3$-hybridization with a tetrahedral configuration formation. Such structural variance was fully confirmed as the peak shifted from 247 nm ($\text{sp}^2$ state) to 274 nm ($\text{sp}^3$ state) in the pH-dependent UV–Vis absorption spectra (Fig. S1). Such charge transfer induced configuration changes based on the electrostatic attraction provided a solid and ultrasensitive probe to the $\text{SO}_4^{2-}$ ion detection in our SERS chip strategy. Furthermore, due to the variable coordination of 4-MPBA, the sensing configuration was probably related to the concentrations of sulfates [32]. Therefore, it is very likely that the 4-MPBA probe coordinates with one $\text{SO}_4^{2-}$ ion when the chip is exposed to a low concentration of $\text{SO}_4^{2-}$ ion, while at high concentrations of sulfates, the 4-MPBA probe simultaneously coordinate with multiple $\text{SO}_4^{2-}$ ions.

Characterization of Ag NPs based SERS chip

The glass coverslip and Ag NPs were employed as the support and signal enhanced media for our SERS chip development, respectively. To easily operate the protocol, a layer of APTES molecules was first modified onto the hydroxylated glass surface for providing $–\text{NH}_2$ groups to immobilize Ag NPs. Therefore, negatively charged Ag NPs were easily grafted on the surface of coverslip at room temperature by strong Ag–N bonds. According to the UV–Vis absorption spectrum and TEM morphology as reproduced in Fig. 3a, b, respectively, the as-synthesized Ag NPs were not clustered or stacked, and displayed a strong characteristic peak attributed to LSPR at 407 nm. Besides, the statistical analysis on Ag NPs showed a relatively uniform distribution in particle size with a mean diameter of 41.01 ± 4.70 nm (Fig. 3c). Under the planar interactions from $–\text{NH}_2$ groups, the immobilized Ag NPs should be uniformly patterned as a monolayer on the glass surface. Recorded SEM morphologies of the chip clearly confirmed our speculation (Fig. 3d). The Ag NPs on the chip presented as a uniformly packed monolayer.

![Fig. 2. Schematic illustration for the coordination reaction of 4-MPBA and the quantitative sensing mechanism for the 4-MPBA modified SERS chip in sulfate-containing solutions](image)
Moreover, the average distance between Ag NPs on the chip was statistically calculated at ca. 31.4 nm (Fig. S2).

To confirm the recognition activity of our SERS chip, the Raman spectra, measured with 532 nm excitation for solid 4-MPBA and the 4-MPBA adsorbed on the SERS chip, were shown in Fig. 4a. It can be easily observed that the band at 2563 cm⁻¹, which was attributed to the S–H stretching vibration (ν_SH) of 4-MPBA, completely disappeared from the Raman spectra after the 4-MPBA molecules absorbed with Ag NPs. Such observation was fully consistent with the previous study [34]. Meanwhile, it clearly confirmed that the 4-MPBA molecules were successfully grafted onto Ag NPs through strong Ag–S bond. In addition, the C–S–H bending band (β_CSH) around 911 cm⁻¹ was invisible in the SERS spectra (line II in Fig. 4a), also proving the formation of Ag–S bond [33]. The detailed band assignments for 4-MPBA were shown in Table S1.

**Effects of operation conditions on the chip sensing**

To test the feasibility of our SERS chip on sensing the SO₄²⁻ ion, 4-MPBA functionalized chips were immersed into a SO₄²⁻ aqueous solution (1.0 × 10⁻³ M) to investigate the adsorption capacity of 4-MPBA on SO₄²⁻ ion, and the corresponding SERS spectra were measured. As shown in Fig. 4a, several strong bands of 4-MPBA, i.e., 1160, 1247, and 1610 cm⁻¹, could easily be observed. Interestingly, a new and solid peak appeared at 1382 cm⁻¹ in the SERS spectrum after the chip being immersed into SO₄²⁻ aqueous solution (line III in Fig. 4a). According to the recognition
between boric acid and $\text{SO}_4^{2-}$ ion, it was reasonable to assign the band at 1382 cm$^{-1}$ to the vibration mode of the B–O–S bond. Furthermore, it was highly sensitive to the $\text{SO}_4^{2-}$ ion, and a high-intensity peak for lower concentrations of the $\text{SO}_4^{2-}$ ion still could be seen in the Raman spectroscopy. Thus, the band at 1382 cm$^{-1}$ could be rationally chosen for subsequent quantitative sensing of the $\text{SO}_4^{2-}$ ion.

For the boronic acid, it was noted that the hydroxyl ion will combine with it and make the molecular structure conversion from a planar structure of $\text{ArB(OH)}_2$ into a tetrahedral configuration of $\text{ArB(OH)}_3^-$ (Fig. S3). Thus, the pH value of the system should be another key factor for the operation of our SERS chip. Figure 4b depicted the Raman spectra of SERS chips after immersion in the sulfate solutions (10–3 M) with different pH environments. As expected, the characteristic peak at 1382 cm$^{-1}$ was always visible as the pH varied from 5 to 11, and was especially noticeable under the neutral condition, i.e., pH = ca. 7.0. It should be stated that, when the sensing chip was operated in an acid environment, hydrogen ions will easily induce the 4-MPBA to stabilize in the $sp^2$-hybridized state, which made it difficult to fully carry out the coordination reaction between $\text{SO}_4^{2-}$ ion and boron atoms. Under alkaline environments, the $\text{SO}_4^{2-}$ ion can combine with hydroxide ions easily through hydrogen bonds, decreasing the concentration of free $\text{SO}_4^{2-}$ ion in the solution. On the other side, the boric acid groups were more inclined to combine with the free hydroxide ion to form $\text{ArB(OH)}_3^-$ with a stable tetrahedral structure in an alkaline environment. Such previous speculations were evidently confirmed from the obtained Raman spectra of the SERS chip immersed in the aqueous solutions with different pH values. As shown in Fig. S4, the band at 998 cm$^{-1}$, which was assigned to the in-plane mode of the tetrahedral configuration of $\text{ArB(OH)}_3^-$, clearly increased with the pH increasing from 5 to 11.

In addition to the measured SERS spectra, the transformation was also confirmed by the measurements of UV–Vis absorption spectra of 4-MPBA. As shown in Fig. S1A, a strong absorption band of 4-MPBA was clearly located at 247 nm under acidic environment (pH = 5), while, with the increase of pH value, the absorption band gradually red-shifted to 274 nm. This variance indicated that the 4-MPBA were transformed into $\text{ArB(OH)}_3^-$ with the introduction of hydroxide ions. It was worth emphasizing that when the pH was located at 6–7 for aqueous solutions of sulfates, 4-MPBA would transform into a stable tetrahedral structure through its own hydrolysis reaction with $\text{SO}_4^{2-}$ ion, instead of the introduction of external hydroxide ions. Therefore, the chip sensing system was decided to operate under a neutral condition, i.e., the pH value was ca. 7, for a more sensitive and specific sensing of the $\text{SO}_4^{2-}$ ion.

**Selectivity and anti-interference of the sensing system**

To evaluate the selectivity and specificity of our SERS chip strategy, various kinds of anions, i.e., $\text{Cl}^-$, $\text{Br}^-$, $\text{NO}_3^-$, $\text{NO}_2^-$, $\text{SO}_3^{2-}$ and $\text{H}_2\text{PO}_4^-$ ions, were employed as interference agents to test the recognition performance under the same assay conditions (Fig. 5a). As expected, even at a higher concentration (10$^{-2}$ M), the Raman spectra of SERS chip only respond to the $\text{SO}_4^{2-}$ ion, and for other anions, the characteristic peak at 1382 cm$^{-1}$ was almost invisible. First of all, for anions with a similar tetrahedral structure, such as the $\text{H}_2\text{PO}_4^-$ ion, the poor response can be attributed to the greater hydration energy [35]. Moreover, for the other
Highly sensitive sensing and quantitative detection of sulfate ion with a SERS chip—based on…

To further evaluate the SERS chip system for accurate identification and sensing of the $\text{SO}_4^{2-}$ ion in the presence of other interfering analytes, a series of interference experiments were performed. As illustrated in Fig. 5b, the obtained ratiometric values ($A$) were undisturbed and always keep constant even though the interfering ions were separately mixed with $\text{SO}_4^{2-}$ ion with a five-fold higher level. Such results clearly indicated that our SERS chip sensing system had reliable specificity and would not be readily interfered by the other anions, that is, the conventional interfering ions had almost no effect on the detection of $\text{SO}_4^{2-}$ ion when operation our SERS chip method.

**Quantitative sensing and detection of the SO$_4^{2-}$ ion**

To evaluate the performance of as-prepared SERS chip on in-site quantitatively sensing the $\text{SO}_4^{2-}$ ion, a series of Raman spectra were measured by introducing different concentrations of $\text{SO}_4^{2-}$ ion aqueous solution onto the surface of the SERS chip (Fig. 6a). Moreover, to eliminate the stochastic errors caused by the inhomogeneity of the SERS chip, the strongest characteristic peak at 1070 cm$^{-1}$, attributed to the plane deformation of C–H on the benzene ring [36], was chosen as an internal standard. Therefore, in our strategy, a ratiometric signal ($A$) of two bands at 1382 and 1070 cm$^{-1}$ was constructed for the quantitative evaluation of $\text{SO}_4^{2-}$ ion based on the following equation:

$$A = \frac{I_{1382}}{I_{1070}}$$

Here, $I_{1382}$ and $I_{1070}$ were the SERS intensities at the bands of 1382 and 1070 cm$^{-1}$, respectively.

According to Eq. (1), the quantitative curve of the $\text{SO}_4^{2-}$ ion was also plotted by monitoring the changes of ratiometric signal $A$. It can be easily found that the peak at 1382 cm$^{-1}$ displayed an obvious intensity dependence on the concentrations of the $\text{SO}_4^{2-}$ ion from $10^{-2}$ to $10^{-8}$ M (Fig. 6a). Moreover, calculated curve indicated that the $A$ values were polynomially correlated with the logarithmic $\text{SO}_4^{2-}$ ion (Fig. 6b). Interestingly, the $A$ values have a positive linear correlation within the concentration range from $10^{-4}$ to $10^{-8}$ M (inset of Fig. 6b).

Based on the above observations, it was reasonable to speculate that at a higher concentration of $\text{SO}_4^{2-}$ ion, i.e., $> 10^{-4}$ M, the boron atom of 4-MPBA probe may interact with multiple $\text{SO}_4^{2-}$ ions similar with the sensing on fluorion [32]. In addition to the intensity variances, from the brown line in Fig. 6a, a clear Raman characteristic peak at 1382 cm$^{-1}$ can be seen at $10^{-8}$ M. This phenomenon indicated that our SERS chip possesses an extremely high sensitivity compared to conventional methods. Notably, the lowest detectable concentrations for $\text{SO}_4^{2-}$ ions were superior to many other previously published experimental methods (Table S2), and significantly lower than the WHO specified value for the $\text{SO}_4^{2-}$ ion (2.6 mM) in drinking water.

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**Fig. 5** The specificity and anti-interfered performance from different anions during the SERS chip operation. a Raman spectra of the SERS chip on sensing different anions commonly found in the environment.

b Variances about the ratiometric $A$ values for an anions mixture. The concentrations for interfering anions and $\text{SO}_4^{2-}$ ion were 50 μM and 10 μM, respectively.
In addition, the assessment on reproducibility based on 25 chips as-prepared in 5 batches indicated that the relative standard deviation (RSD) of the peak ratio ($A_{1382}/A_{1070}$) was ca. 3.72%. Such results implied that our SERS chip approach had a satisfactory reproducibility on quantitative evaluation of $SO_4^{2−}$ ion.

### Sensing of $SO_4^{2−}$ ion in actual samples

#### Tap water

As we all know, most of anionic pollutants were discharged into drinking water along with waste gas and/or wastewater, and therefore, whether the SERS chip system can be used to detect $SO_4^{2−}$ ion in actual environment was quite crucial. In this topic, tap water was employed, and three pre-decided samples spiked with standard $K_2SO_4$ salt were obtained. Subsequently, the SERS spectra of tap water samples were collected following pre-decided operation conditions (Fig. S6), and the contents and recoveries of $SO_4^{2−}$ ion in samples were derived from the pre-built standard curve as shown in Fig. 6b. Results were summarized in Table 1, it can be seen that the recoveries ranged from 97.1 to 105.0%, and the RSDs were lower than 8.0% for all three samples.

#### Beer

The addition of the sodium metabisulfite in beer and the metabolism of yeast during fermentation will generate $SO_2$. And the perhydroxyl radical (·OOH) will be generated during the storage process, and the $SO_2$ was oxidized to $SO_4^{2−}$ ion and existed in the beer. Therefore, the SERS sensing system was further applied for the detection of $SO_4^{2−}$ ion in beer. Beer samples were diluted to reduce interference from organic molecules and filtered to extract $SO_4^{2−}$ ion. From the spectra in Fig. S6, it can be found that the characteristic peaks at 1070 cm$^{-1}$ and 1382 cm$^{-1}$ were hardly shift, proving that the soluble components in beer would not interfere the detection

### Table 1 Evaluation results on sensing $SO_4^{2−}$ ion in tap water, beer, and bottled mineral water

| Sample                  | Spiked (mol/L) | Found (mol/L) | Recovery (%) | RSD (%) |
|-------------------------|----------------|---------------|--------------|---------|
| Tap water               | $1 \times 10^{-4}$ | $1.05 \times 10^{-4}$ | 105.0        | 7.68    |
|                         | $1 \times 10^{-5}$ | $1.01 \times 10^{-5}$ | 101.0        | 5.09    |
|                         | $1 \times 10^{-6}$ | $9.81 \times 10^{-7}$ | 98.10        | 2.91    |
| Beer                    | 0              | $6.02 \times 10^{-7}$ | –            | 5.78    |
|                         | $1 \times 10^{-6}$ | $1.75 \times 10^{-6}$ | 109.24       | 7.68    |
|                         | $1 \times 10^{-5}$ | $1.04 \times 10^{-5}$ | 98.37        | 10.34   |
| Bottled mineral water  | 0              | $1.09 \times 10^{-7}$ | –            | 10.17   |
|                         | $5 \times 10^{-7}$ | $6.05 \times 10^{-7}$ | 99.20        | 6.56    |
|                         | $1 \times 10^{-6}$ | $1.21 \times 10^{-6}$ | 110.12       | 8.33    |
of $\text{SO}_4^{2-}$. As shown in Table 1, the concentration of $\text{SO}_4^{2-}$ ion in beer was measured to be $6.02 \times 10^{-7}$ M, recoveries were ranged from 109.24 to 98.37%, and RSDs was less than 11%.

**Bottled mineral water**

The $\text{SO}_4^{2-}$ ion in bottled mineral water was further measured. The concentration of $\text{SO}_4^{2-}$ ion in mineral water was $1.09 \times 10^{-7}$ M. At the same time, a high recovery rate (99.20–110.12%) was obtained, and the RSDs were also less than 11%. These results further illustrated that this SERS chip had a good sensitivity and accuracy for the detection of $\text{SO}_4^{2-}$ ion in complex sample matrices.

**Evaluation of the $\text{SO}_3^{2-}$ ion**

Interestingly, in addition to the sulfate anion, this SERS chip system also maintains a potential to evaluate the $\text{SO}_3^{2-}$ ion. Different with direct sensing on sulfates, the $\text{SO}_3^{2-}$ ion should be transferred into $\text{SO}_4^{2-}$ ion through an oxidation reaction before evaluation. Figure 7 showed the oxidation time-dependent variance for the characteristic peak at 1382 cm$^{-1}$ in a $\text{SO}_3^{2-}$/SO$_4^{2-}$ ions co-existed aqueous solution. The $\text{SO}_3^{2-}$ and SO$_4^{2-}$ ions were mixed at a ratio of 1:100, i.e., $10^{-5}$ M: $10^{-3}$ M, and then, excess nitric acid was added prior to the Raman spectra measurements. In Fig. 7, it can be easily seen that the SERS chip showed a good response to $\text{SO}_4^{2-}$ ion, and subsequently, the intensity of characteristic peak gradually increased as the extension of oxidation time from 0 to 15 min. Such variance was consistent with our above investigations. However, the characteristic peak displayed a slight shift from 1379 to 1382 cm$^{-1}$ probably due to the attractions between 4-MPBA molecules and $\text{SO}_3^{2-}$ ion. Notwithstanding, based on pre-decided standard curve for $\text{SO}_4^{2-}$ ion and the subtraction calculation, the recovery of $\text{SO}_3^{2-}$ ion was calculated to be 102.2% for above sample. These acceptable results revealed that our chip sensing system also has the potential to quantitatively evaluate $\text{SO}_3^{2-}$ ion.

**Conclusions**

In summary, a novel SERS chip strategy based on the attraction of Lewis acid of 4-MPBA probe for sensitively and quantitatively sensing $\text{SO}_4^{2-}$ ion was proposed in this study. Our SERS chip technology exhibited several excellent advantages over previous techniques on the detection of $\text{SO}_4^{2-}$ ion, e.g., simple operations, high sensitivity, and strong specificity. Based on the quantified ratio between characteristic peaks of $\text{SO}_4^{2-}$ ion and 4-MPBA probe, i.e., 1382 and 1070 cm$^{-1}$, respectively, the SERS chip displayed a prominent performance on direct evaluation of $\text{SO}_4^{2-}$ ion in tap water with the level down to 10 nM. It was over 4 orders of magnitude lower than that prescribed by WHO for the $\text{SO}_4^{2-}$ ion (2.6 mM) in drinking waters. In addition to the detection of $\text{SO}_4^{2-}$ ion, the SERS chip also displayed potential applicability on the evaluation of $\text{SO}_3^{2-}$ ion. In light of these findings, this facile, accurate, and reliable SERS chip strategy undoubtedly provide a promising alternative way for quantifying trace amounts to $\text{SO}_4^{2-}$ and $\text{SO}_3^{2-}$ ions in actual water samples and/or in-site monitoring of environmental pollution of sulfates.

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