



Surface-enhanced Raman scattering of perchlorate on cationic-modified silver nanofilms – Effect of inorganic anions



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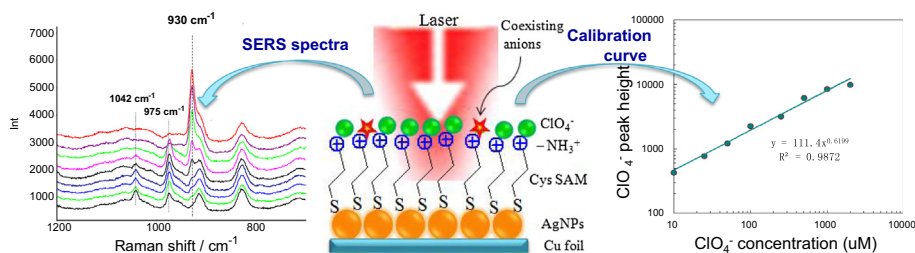
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HIGHLIGHTS

- Cationic thiol modified SERS substrates were fabricated for selective detection of ClO_4^- .
- Effects of common anions on ClO_4^- SERS spectra were investigated and analyzed by modeling.
- Competitive interaction mechanisms of the anions with the SERS substrate were discussed.
- Quantitative SERS detection of ClO_4^- in the presence of common anions was demonstrated.
- The study will help developing a robust SERS substrate for aqueous ClO_4^- detection in matrix.

GRAPHICAL ABSTRACT



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ABSTRACT

Surface-enhanced Raman scattering (SERS) has emerged as one of the most sensitive spectroscopic analysis methods for the detection of environmental contaminants in water, including perchlorate (ClO_4^-). However, as with other commonly used analytical techniques, analysis of realistic environmental samples by SERS presents a challenge due to complex chemical components coexisting in the samples. In this work, we investigated the influence of inorganic anions (particularly oxyanions) on SERS spectra of ClO_4^- using a cationic thiol modified silver nanofilm substrate (Cys–Ag/rCu). The results show that the anions present in the samples did not shift the ClO_4^- characteristic band positions, but did decrease signal intensities due to their competitive binding with the $-\text{NH}_3^+$ groups of cationic thiol molecules immobilized on the substrates. The pH changes caused by both the dissociation of H_2PO_4^- and the hydrolysis of HCO_3^- may also play a non-negligible role. The selectivity of the Cys–Ag/rCu substrate towards these anions was determined to be in the following order: $\text{ClO}_4^- > \text{SO}_4^{2-} > \text{HCO}_3^-$, $\text{NO}_3^- > \text{Cl}^- > \text{H}_2\text{PO}_4^-$, indicating preferential adsorption of ClO_4^- ions. In the solutions with multiple anions present, the ClO_4^- SERS spectra were affected simultaneously by all the coexisting anions. Calibration curves with very good linear relationships were successfully obtained, demonstrating the great potential of quantitative detection of aqueous ClO_4^- in the matrix.

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Introduction

Perchlorate (ClO_4^-) is a widely used component of solid fuel missile and rocket propellants, explosives, and pyrotechnics [1]. It has recently emerged as a widespread environmental contaminant

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found in foods, milks, drinking water, groundwater, and soils in many countries including the United States [1–4]. ClO_4^- is believed to disrupt the thyroid function by inhibiting the uptake of iodide, affecting the production of thyroid hormone and possibly causing mental retardation in fetuses and infants [4,5]. The U.S. Environmental Protection Agency (EPA) is developing a proposed national primary drinking water regulation for ClO_4^- , and has established an Interim Drinking Water Health Advisory limit of 15 $\mu\text{g/L}$ (ppb) [6]. This concentration limit will definitely have a significant impact on the management and remediation of perchlorate-contaminated sites and public water systems, and will require technological innovations for sensitive, rapid, and inexpensive field analyzers. Currently used techniques for ClO_4^- analyses include mainly ion chromatography (IC), electrospray ionization mass spectrometry (ESI-MS), IC-MS and ion-selective electrodes (ISE) [7]. However, these methods either require large, expensive equipment, time-consuming and complex sample preparation, well-trained users, or are associated with issues of sensitivity and selectivity, making them not suitable for field applications. Therefore, there is a critical need for the development of a rapid, simple and cost-effective portable chemical analyzer for on-site identification and quantification of trace-level ClO_4^- in environmental water.

Surface-enhanced Raman scattering (SERS), as one of the most sensitive spectroscopic analysis methods, has been extensively investigated for chemical and biological sensing [8–17] including the possibility of detecting single molecules [18–20]. In particular, the combination of the SERS technique with commercially available portable/handheld Raman systems has shown great potential to meet the criteria of field assays of environmental pollutants including ClO_4^- ions [21–26]. It is well known that only the molecules which adsorb chemically or physically onto nanostructured substrates of noble metals (mostly Ag or Au) produce a significant SERS effect. The SERS detection of trace level ClO_4^- in water appears to be very difficult due to its high water solubility and extremely weak sorption tendency on these metals [27,28]. To solve this problem, two approaches have been used. One is to measure SERS spectra using samples air-dried on planar SERS substrates to deposit perchlorate onto nanostructured Ag or Au surfaces [22,29]. Another approach has been developed to chemically modify the SERS substrates, trapping and concentrating ClO_4^- anions onto Ag or Au surfaces [7,30–36]. The modification reagents commonly bear positively-charged groups such as $-\text{NH}_3^+$, $-\text{NH}(\text{CH}_3)_2^+$ and $-\text{N}(\text{CH}_3)_3^+$. For example, we recently developed a cysteamine hydrochloride (Cys) modified Ag nanofilm deposited on a roughened Cu foil (Cys–Ag/rCu) for rapid and sensitive SERS analysis of aqueous ClO_4^- without the need for drying. The Cys ($\text{HSCH}_2\text{CH}_2\text{NH}_2 \cdot \text{HCl}$) is a cationic thiol. The Cys molecules formed a self-assembled monolayer (SAM) on the surface of the Ag/rCu nanofilm, and their protonated amino groups $-\text{NH}_3^+$ make the substrate surface positively charged, which promotes the adsorption and enrichments of the negatively charged ClO_4^- ions. Thus, the SERS signal of ClO_4^- can be enhanced dramatically, enabling sensitive SERS measurement to be accomplished immediately once the aqueous ClO_4^- samples are applied onto the Cys–Ag/rCu film.

However, as with other commonly used techniques, analysis of realistic environmental samples by SERS presents a challenge because of complex chemical components coexisting in the samples that interfere with the analysis [30,36,37]. Moreover, many of the coexisting components are present in higher concentrations than the analytes of interest, making the detection more complicated. Therefore, it is very important to account for the interactions of both the interferents and the analytes with the SERS substrates as well as the effect of the interferents on the SERS detection of the analytes. In this work, we systematically investigated the SERS spectra of ClO_4^- solutions in the presence of common inorganic anions (especially oxyanions), typically including Cl^- , NO_3^- , SO_4^{2-} ,

HCO_3^- and H_2PO_4^- using the positively-charged Cys–Ag/rCu substrates and further analyzed the effects of these inorganic anions on the SERS detection of ClO_4^- . Also, the interaction mechanisms were examined in order to gain a better understanding on the effect of the anions on the ClO_4^- SERS spectra and aid in development and optimization of the sensitive and selective SERS substrates for the ClO_4^- detection in environmental water.

Experimental

Materials

Copper foils (Cu, 10 cm \times 10 cm in area, 0.25 mm in thickness, 99.99%) were purchased from Goodfellow (Oakdale, PA, USA). Sodium perchlorate ($\text{NaClO}_4 \cdot \text{H}_2\text{O}$) was purchased from EM Science (Cherry Hill, NJ, USA). Silver nitrate (AgNO_3) and cysteamine hydrochloride were obtained from Fisher Scientific (Fair Lawn, NJ, USA) and Sigma–Aldrich (Milwaukee, WI, USA), respectively. All other chemicals including sodium chloride (NaCl), sodium nitrate (NaNO_3), sodium sulfate (Na_2SO_4), sodium bicarbonate (NaHCO_3) and sodium phosphate monobasic (NaH_2PO_4) were analytical grade and purchased from Sigma–Aldrich (Milwaukee, WI, USA) or Fisher Scientific and used as received. Deionized (DI) water with a resistivity of 18.2 M Ω cm (Millipore Milli-Q System) was used throughout the experiments.

Preparation of Cys–Ag/rCu substrates

The Cu foils were cut into pieces of 10 cm \times 2.5 cm and washed consecutively with acetone and ethanol to remove organic impurities. To obtain fresh and roughened Cu surfaces, the cleaned Cu foils were etched by immersion in a 1:1 (V:V) nitric acid (HNO_3) solution for ~ 20 s. After rinsing thoroughly with DI water, the roughened Cu (rCu) foils were kept in a 1% sulfuric acid (H_2SO_4) solution to prevent the rCu foil from undergoing excessive oxidation. The deposition of the Ag nanofilm and the subsequent Cys modification followed an optimized procedure reported in our previous work [34]. Briefly, a piece of rCu foil was immersed into a 50 mL aqueous solution containing 2.5 mM AgNO_3 for 5 min at room temperature. After rinsing with copious amounts of DI water and dried under a stream of compressed nitrogen gas, the resulting Ag/rCu film was incubated in a freshly prepared 5 mM Cys solution for 3 min to allow the formation of the SAM on the Ag surface. The Cys–Ag/rCu substrate was obtained after DI rinsing and N_2 drying, and kept in an enclosed container prior to the SERS measurements.

Instruments and methods

The deposition of the Ag nanofilm on the roughened Cu surface was confirmed by images (Fig. 1S in Supplementary Data) obtained with a field-emission scanning electron microscope (FESEM) (LEO 982, LEO Electron Microscopy Inc., Thornwood, NY) operated at an accelerating voltage of 7 kV and working distance (WD) of 5 or 6 mm. The Raman spectra were collected in high resolution mode on a Thermo Nicolet Almega XR Dispersive Raman Spectrometer (Thermo Fisher Scientific Inc., USA) equipped with a CCD detector, an optical microscope and a digital camera, and a 780 nm laser line with a maximum power of 32 mW (16 mW was applied in the experiments). All measurements were conducted using a 180° backscattering geometry. A 10X microscope objective was used, providing a laser spot size of 3.1 μm .

Aqueous ClO_4^- samples in a concentration range of 1–2000 μM were prepared by diluting a stock solution of 0.1 M with DI water. Solutions of Cl^- , NO_3^- , SO_4^{2-} , HCO_3^- and H_2PO_4^- were prepared by diluting their sodium salt solutions of 0.1 M with DI water, respec-

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