CARS MICROSCOPIC MEASUREMENT OF MULTIPLE ION CONCENTRATION IN A CHEMICAL REACTION

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ABSTRACT
A non-intrusive technique for ion concentration measurements in electrolyte solutions was developed. The present study employs coherent anti-Stokes Raman scattering (CARS) which enables chemically-specific concentration measurement with high spatio-temporal resolution. A CARS microscopic system was developed to focus on a specific wavenumber of the signal for each solution. With the developed system, a quantitative relationship between CARS intensity ratio and ion concentration for each solution was obtained.

KEYWORDS: Non-intrusive measurement, CARS, Ion concentration, Electrolyte solution

INTRODUCTION
When miniaturizing fluidic systems, the electrically-charged channel wall and material interface have significant electrochemical influence on the flow structure and chemical properties of the solutions. Therefore investigation of the ion motion is required to realize efficient control of the chemical reactions. Laser-induced fluorescence (LIF) [1] is a typical technique for ion concentration measurements, but the fluorescent dye adversely influences the sample solution. Recently, a non-intrusive and chemically-specific approach using spontaneous Raman scattering was reported [2]. However, the signal intensity from the Raman process is relatively weak and lengthens the time to acquire data. In order to address this problem, the present study focused on coherent anti-Stokes Raman scattering (CARS) microscopy which realizes much higher sensitivity, non-intrusiveness and chemically-specific sensing. The final goal of the present study is to analyze mixing and reaction processes in microfluidics based on ion concentration measurements by detecting the CARS signal which provides quantitative information on the concentration at the focal point of the laser beam excitation (as shown in Figure 1).

Figure 1: Schematic concept of CARS microscopy for sensing the ion concentration distribution in a chemical reaction.

THEORY
When an incident laser beam $\nu_i$ is irradiated to the sample, light gets inelastically scattered with frequencies $\nu_i - \nu_R$ and $\nu_i + \nu_R$, which are called Stokes Raman Scattering and anti-Stokes Raman scattering, respectively. The difference of frequency from the incident light $\nu_R$ is called Raman shift and its value depends on the structure of the sample molecules. Since Raman scattering derives from vibrational motion of the molecules, its signal intensity describes the sample condition and its properties such as temperature and concentration. Shown in Figure 2 are the spectra of spontaneously

![Figure 2: Spontaneous Raman spectra of the (a) NH₄Cl solution and (b) Na₂SO₄ solution.](image_url)

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emitted signals from the solutions used in this study. The NH$_4$Cl solution has its specific peak at 3400 cm$^{-1}$ and Na$_2$SO$_4$ at 982 cm$^{-1}$, respectively, and the signal intensities depend on their concentrations. These spectra show that by focusing on the intensity in a particular wavelength of the scattered light, chemically-specific measurement of the ion concentration can be conducted.

Coherent anti-Stokes Raman scattering is a nonlinear Raman process with stimulated emission by ultrashort pulsed laser. CARS is generated by two light sources, the Stokes beam with frequency $v_1$ and the pump beam with frequency $v_2$. The vibrational resonance of the sample is maximized when the frequency difference of the two beams coincide with the frequency of the Raman-active molecular vibration. Subsequent incidence of the probe beam with frequency $v_1$ results the generation of CARS signal with frequency $2v_1-v_2$. Since signal-to-noise ratio of CARS is superior to spontaneous Raman and it also enables chemically-specific measurement, CARS was employed to realize ion concentration measurement in this study.

**EXPERIMENTAL SETUP**

The experimental setup is shown in Figure 3. A Ti:Sapphire femtosecond pulsed laser with a wavelength of 800 nm was used as the excitation source. The laser light was partially introduced into an optical parametric oscillator and its wavelength was converted for another incident light. For the measurement of NH$_4$Cl, the wavelength of pump beam ($v_1$), and Stokes beam ($v_2$) were 800 nm, and 1100 nm, respectively. For the Na$_2$SO$_4$ measurement, the pump beam ($v_1$), and Stokes beam ($v_2$) were set to 741 nm and 800 nm. In order to generate the CARS signal, two excitation lasers were synchronized temporally by changing the optical length with a micromotion stage and overlapped coaxially by a dichroic mirror. The overlapped laser was focused into a solution-filled channel with an objective lens. The CARS arising from the solution passed through an objective lens, a filter block to discriminate signal from the excitation beams and detected by a EM-CCD camera ($512 \times 512$ pixels$^2$, $16 \times 16$ μm$^2$/pixel, 16 bits) equipped with a spectrometer. Spectral resolution of the system was determined to be approximately 14.4 cm$^{-1}$. The CARS signal was acquired on two microscopes simultaneously to record the reference value from the solution with 1 mol/L on the unilateral microscope. Then the CARS intensity ratio was computed to eliminate the influence of intensity fluctuation of the excitation beams. Table 1 shows the properties of the measured solutions. The solutions were set in the channel illustrated in Figure 4. The top and bottom wall of the channel was made of borosilicate glass and side wall was made of PDMS (poly-(dimethylsiloxane)). The exposure time was set to 30 ms, and 100 images were acquired to temporally average for each measurement.

**RESULTS AND DISCUSSION**

Figure 5 shows the spectra of the CARS signal obtained from each electrolyte solution and water. From these results,
an increase in signal intensity can be observed for 3400 cm\(^{-1}\) and 982 cm\(^{-1}\). In this study, the total intensity within FWHM (full width at half maximum) of each spectrum was used as signal intensity of CARS signals. To obtain the quantitative relationship between the CARS intensity ratio and the ion concentration, CARS signals at wavenumbers 3400 cm\(^{-1}\) and 982 cm\(^{-1}\) were measured from NH\(_4\)Cl solutions (1 - 4 mol/L) and Na\(_2\)SO\(_4\) (0 - 1 mol/L) solutions, as shown in Table 1. Figure 6 shows the measurement results. For each solution, increased CARS intensity was observed at the intended Raman shift with increased ion concentration. Measurement of each ion concentration can be realized by applying these calibration curves.

**CONCLUSION**

For the investigation of ion motion inside microfluidic devices, development of a CARS ion concentration measurement in electrolyte solution was conducted. Spontaneous Raman spectra showed the chemically-specific signal at particular wavenumbers, 982 cm\(^{-1}\) and 3400 cm\(^{-1}\) and CARS spectra were acquired at these wavenumbers for each solution. The influence from the fluctuation of the incident laser beam was eliminated by computing the CARS intensity ratio from the signal intensity obtained from two microscopes. By acquiring a relationship between the CARS intensity ratio and the ion concentration, the increase in the signal intensity ratio was confirmed for both solutions. According to these results, focusing on a specific wavenumber for each solution, the possibility to measure its ion concentration of each solution was demonstrated.

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