Resonant surface-enhanced infrared absorption spectroscopy utilizing gold nanoslit array stuructures

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Infrared (IR) light resonates with a variety of molecular vibrations, making it a powerful probe for chemical species. Surface-enhanced IR absorption spectroscopy (SEIRAS), where plasmonic near-fields are utilized to amplify the light-molecule interaction, enables surface-selective detection with unprecedent sensitivity. One of the promising applications of SEIRAS is monitoring electrochemical reactions (ECR) [1]. To date, SEIRAS has been utilized for ECR using metal nanoparticles (NPs) on an attenuated total reflection (ATR) prism. The NPs produce plasmon resonances with a broad absorption mainly in the visible range, which limits the sensitivity in the IR range. Here, we aim at developing SEIRAS utilizing IR-resonant metal nanoslit structures toward highly-sensitive monitoring of ECR. The nanoslits have advantages over nanoantennas in larger hotspot volumes and conductivity as an electrode [2]. In this work, we report on the design of the nanoslits and the evaluation of the fabricated nanoslits.

Our target vibrational mode is anti-symmetric stretching of carbon dioxide at 2343 cm^{-1}. Finite-difference time-domain simulations are performed to design the nanoslit arrays. Figure 1 illustrates the near-field enhancement spectrum and the near-field distribution of designed nanoslit arrays. A remarkable near-field enhancement of approximately 50-fold is found at the target frequency. Based on the design, we fabricate the nanoslit arrays with electron beam lithography and argon-ion milling processes. Figure 2 shows the optical microscope image and the reflectance spectra of the fabricated nanoslits. In the reflectance spectra, a dip structure is observed when excited with parallel polarized light to the long slit axis, whereas no dip is observed when excited with perpendicularly polarized light. This indicates the fabricated nanoslits have the plasmonic resonance. The broader bandwidth compared with the simulation can be due to the inhomogeneity of the fabricated nanoslits. In the future, we will utilize the fabricated nanoslits to resonant SEIRAS for observing the electrochemical process of CO_2 reduction reactions.

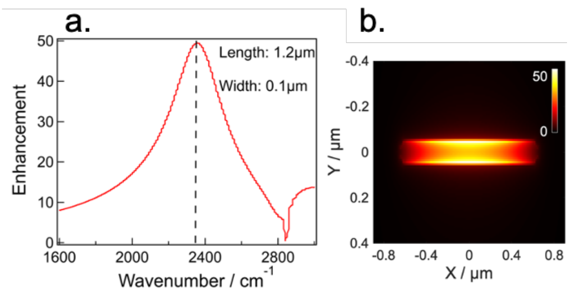

Fig. 1 a. The simulated near-field enhancement spectrum and **b.** the near-field distribution of the nanoslits.

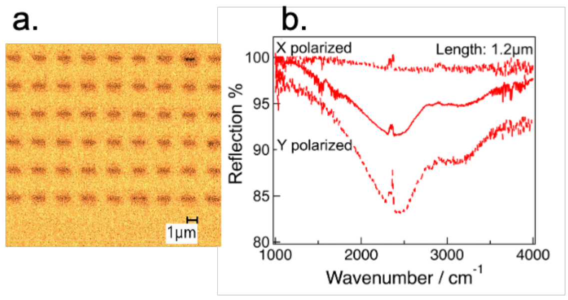

Fig. 2 a. The optical microsope image and **b.** the reflectance spectra of the nanoslits.

[1] R. Kas et al., Chem. Phys. Chem. **20**, 12881 (2019). [2] C. Huck et al., ACS Photonics **2**, 1489 (2015).