Metamaterial-Enhanced Infrared Absorption Spectroscopy

Atsushi Ishikawa^{1,2} and Takuo Tanaka^{2,3}

¹ Department of Electrical and Electronic Engineering, Okayama University, Japan
² Metamaterials Laboratory, RIKEN, Japan
³ Research Institute for Electronic Science, Hokkaido University, Japan

E-mail: a-ishikawa@okayama-u.ac.jp

1. Introduction

Infrared (IR) absorption spectroscopy of molecular vibrations is of importance in material/medical science and security detection, since it provides essential information of the molecular structure, composition, and environment. For the versatile applications in prompt/easy-to-use inspection technologies, direct (far-field) detection of extremely small amounts of molecules is required. Surface-enhanced IR absorption (SEIRA) has been extensively studied and dramatic improvements of the sensitivity by several orders of magnitude were demonstrated using a tailored plasmonic nanostructures [1-5]. Here, we demonstrate background-suppressed resonant SEIRA of a self-assembled monolayer (SAM) chemisorbed on a metamaterial IR absorber [6,7]. Our metamaterial approach allows for a low-background detection scheme with significant plasmonic enhancement, thus further lowering the detection limit of direct IR absorption spectroscopy.

2. Results and Discussions

The metamaterial absorber consisted of 1D array of Au micro-ribbons on a thick Au film separated by an MgF₂ gap layer. Figures 1(a) and 1(b) show a photograph of the sample and its SEM image, demonstrating uniform surface structures over a large sample area. The micro-ribbon structures were designed to exhibit an anomalous IR absorption at ~ 3000 cm⁻¹, which spectrally overlapped with symmetric/anti-symmetric C-H stretching vibrational modes. 16-Mercaptohexadecanoic acid (16-MHDA), shown in the inset of Fig. 1(c), was used as a target molecule, which formed a 21.5-Å thick SAM with their thiol head-group chemisorbed on the Au surface [8].

Figure 1(c) shows FT-IR Reflection-Absorption Spectroscopy (RAS) spectra of a SAM of 16-MHDA molecules on a bare Au surface (top) and on the metamaterial (bottom). For the bare Au case, the spectrum naturally suffered from extremely-low signal quality, thus being hard to detect the respective absorption dips. The metamaterial, on the other hand, exhibited a broad plasmonic absorption at \sim 3000 cm⁻¹ for the p-polarization with the electric field perpendicular to the ribbon. With the molecules in the vicinity of the ribbon structures, their vibrational modes resonantly coupled with the plasmonic modes of the metamaterial. This in turn produced distinct Fano-like anti-resonant peaks within a broad absorption of the metamaterial. Using the SAM packing density of 21.4 Å²/molecule [9], the sensitivity was estimated to be ~ 1.8 attomoles within the diffraction-limited IR beam spot in the RAS measurement.



FIG. 1. (a) Photograph of a metamaterial infrared absorber $(26 \times 26 \text{ mm}^2)$ and (b) its SEM image. (c) FT-IR RAS spectrum of a SAM of 16-MHDA molecules on a bare Au surface (top) and on the metamaterial for different polarizations (bottom). Molecular structure of 16-MHDA [the inset of (c)] exhibited symmetric/anti-symmetric C-H stretching vibrational modes in the shaded region. Fano-like anti-resonant peaks, indicated by the arrows, arose from the resonant coupling between the plasmonic modes of the metamaterial and the molecular vibrational modes.

3. Conclusions

A novel spectroscopic technique based on metamaterial-enhanced IR absorption was demonstrated. The low-background detection scheme with tailored plasmonic enhancement achieved by the metamaterial dramatically improved the sensitivity of direct IR absorption spectroscopy. Our metamaterial approach may open up new avenues for realizing ultrasensitive IR inspection technologies.

Acknowledgements

This work was partly supported by the RIKEN Incentive Research Grant in FY 2013.

References

- [1] M. Osawa et al., J. Phys. Chem. 95, 9914 (1991).
- [2] T. R. Jensen et al., Appl. Spectrosc. 54, 371 (2000).
- [3] J. Kundu et al., Chem. Phys. Lett. 452, 115 (2008).
- [4] F. Neubrech et al., Phys. Rev. Lett. 101, 157403 (2008).
- [5] E. Cubukcu *et al.*, Appl. Phys. Lett. **95**, 043113 (2009).
- [6] N. Liu et al., Nano Lett. 10, 2342 (2010).
- [7] A. Tittl et al., Nano Lett. 11, 4366 (2011).
- [8]A. Gole et al., Langmuir 20, 7117 (2004).
- [9] L. Strong et al., Langmuir 4, 546 (1988).