Oxide surface functionalization for infrared plasmonic sensing

Kai Chen[1], Thang Duy Dao[1], Satoshi Ishii[1], and Tadaaki Nagao[1,2]

[1] National Institute for Materials Science, [2] Hokkaido University
E-mail: nagao.tadaaki@nims.go.jp

Surface-enhanced infrared absorption (SEIRA) spectroscopy employs noble metal nanoparticles or nanostructures to enhance the characteristic absorption spectra of certain molecules. One of the critical steps is to achieve robust surface functionalization of the plasmonic nanostructures facilitating further functionalization or repeatable sensing performance. Here we explore the application of Al and ITO nanostructures in infrared spectroscopy and demonstrate surface functionalization with phosphonic acid that show strong bonding with oxide surface. We fabricated large-area aluminum (Al) metamaterial perfect absorber (MPA) based on nanosphere lithography (NSL)[1-2]. Near perfect absorption ~97% was achieved at resonance wavelength that is tunable by changing Al disk diameters. We took advantage of the presence of the Al_2O_3 layer and successfully detected presence of the self-assembly monolayer of phosphonic acid on the Al disks[1].

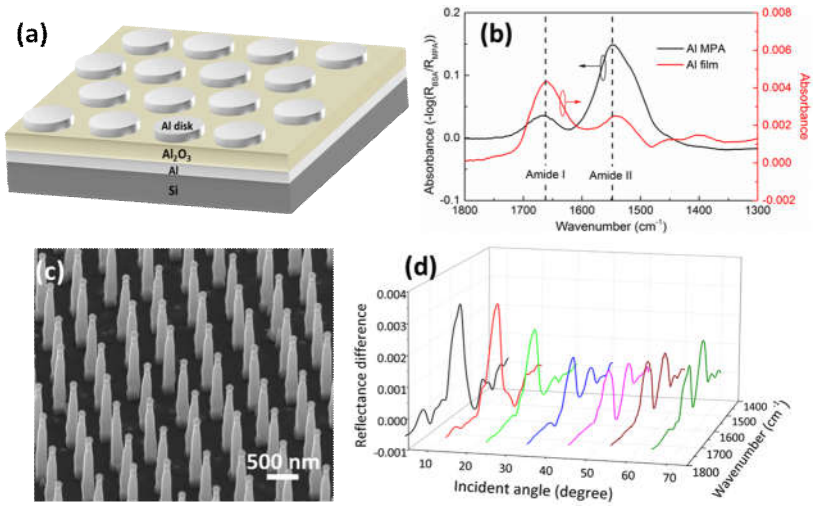

Fig.1 (a) Illustrate of the Al metamaterial perfect absorbers. (b) Absorbance spectra of BSA on Al film (red, right axis) and Al MPA (black, left axis). (c) SEM image of ITO nanorod array (d) Selectively enhanced Amide bands from the attached protein on ITO nanorod arrays.

We also demonstrate surface functionalization of ITO nanorod arrays with phosphonic acid derived biotin molecules and subsequently detection of a monolayer of streptavidin protein. By varying the incident angle, we achieved selective enhancement of certain molecule vibrational modes (Fig. 1d) [3].

In summary, we demonstrate effective and robust surface functionalization of oxide surface with phosphonic acid and demonstrate their applications in biosensing with plasmon-enhanced infrared spectroscopy. The Al MPAs and ITO nanorod arrays are promising for novel and ultrasensitive infrared molecular sensing applications.

Acknowledgements

This work was supported by CREST under the project of "Phase Interface Science for Highly Efficient Energy Utilization", Japan Science and Technology Agency, and also supported by JSPS KAKENHI Grant Numbers 16H06364 and 16K21601.

References

[1] K. Chen, T. Dao, S. Ishii, M. Aono, and T. Nagao, *Adv. Funct. Mater.*, **25**, 6637, (2015)
[2] K. Chen, T. Dao and T. Nagao, *Sci. Rep.*, **7**, 44069, (2017)
[3] K. Chen, P. Guo, T. Dao, S. Li, S. Ishii, T. Nagao and R. Chang, *Adv. Opt. Mater.*, DOI: 10.1002/adom.201700091