Towards Tip-enhanced Nonlinear Raman Spectroscopy & Nanoscopy

Norihiko Hayazawa1,2,3, Kentaro Furusawa1,2, and Satoshi Kawata1,2,3,4
1Nanophotonics Laboratory, RIKEN, 2-1 Hirosawa, Wako, Saitama 351-0198, Japan
2Near-field Nanophotonics Research Team, RIKEN, 2-1 Hirosawa, Wako, Saitama 351-0198, Japan
3CREST, Japan Science and Technology Agency, Kawaguchi, Saitama 332-0012, Japan
4Department of Applied Physics, Osaka University, Suita, Osaka 565-0871, Japan

https://sites.google.com/site/hayazawa/

Our contribution in the CARS session should be extreme spatial resolution in CARS. Yes, we have been working on the development of variety of tip-enhanced near-field spectroscopy and nanoscopy, which can go beyond the classical limit of the spatial resolution, well known as “diffraction limit”. Our research concept is schematically described in Fig. 1 consisting of three optical techniques, near-field optics, vibrational spectroscopy, and nonlinear optics. We have developed several near-field spectroscopic techniques such as fluorescence1, Raman2, TPF3 and CARS4,5. In tip-enhanced CARS based on two narrowband laser pulses (NB-CARS), we have achieved the spatial resolution down to 15nm, which is, to our knowledge, the best spatial resolution ever in CARS nanoscopy (not microscopy anymore).

In this presentation, we show the development of tip-enhanced broadband CARS (BB-CARS) to enhance the spectroscopic coverage of the tip-enhanced CARS nanoscopy. The key technologies involved in TE-BB-CARS can be categorized into two. One is a non-optical feedback system for the tip-sample distance control of a metallic tip, which is essential since a BB light source is apt to interfere with the optical feedback. Another is the suppression of the nonlinear light emissions from both a sample and the metallic tip that become evident as the pulse duration becomes shorter. One of such nonlinear light emissions is four wave mixing (FWM) from a metallic tip itself, which used to be considered as a background of CARS5 but recently gains a renewed interest as a tunable nanoscale light source6. In terms of SNR, either enhancing ‘S’ or reducing ‘N’ is the way to improve the ratio. In the case of ‘S’, there is another ongoing debate7 whether a nonlinear or coherent nature (CARS) can provide a better sensitivity than the spontaneous case (Raman) for a given sample volume. Here we focus on the reduction of ‘N’ by using BB-CARS. Recently, several groups reported the three-color mechanism of BB-CARS that can be used in a time resolved manner for suppressing the nonresonant background8,9. The same idea is also applicable to the background emission from the metallic tip. We employ either fundamental of BB ultrashort laser pulse (~10fs)10 or white light continuum from a PCF. Combined these light sources with our in-house non-optical AFM, we visualize single walled carbon nanotubes for G and D bands, simultaneously.

References