Antenna-assisted surface-enhanced infrared absorption based on nanogaps for ultrasensitive sensors

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Abstract

In this paper we report on an increased vibrational signal enhancement in antenna-assisted surface-enhanced infrared spectroscopy (SEIRS) induced by inter-particle near-field coupling. Nanoantenna dimers with gaps sizes down to 10 nm were prepared by electron beam lithography and afterwards covered with a molecular monolayer of deuterated octadecanethiol as a near-field probe. In our experiments we found an increasing vibrational signal enhancement for decreasing gap sizes demonstrating the additional enhancement induced by nano-sized gaps.

1. Introduction

Infrared (IR) spectroscopy is well suited for a label-free and direct characterization of molecular species. Inconveniently, the analysis of small amounts of molecules, which is of large interest for sensor applications, is hampered by their relative low IR cross-sections. One possibility to overcome this limitation is the use surface-enhanced IR absorption spectroscopy (SEIRS) [1], where huge electromagnetic near-fields provided by plasmonic excitations of metal nanoparticles are employed to enhance signals from molecular vibrations. As shown recently, SEIRS with individual metal nanostructures resonantly tuned to IR vibrational bands of molecular species (nanoantenna-assisted SEIRS) [2,3] has indicated the way towards extreme amplification of the vibrational IR signal (enhancement factor $5x10^5$), which allows sensing with attomolar sensitivity. As known from theory [4], nanoantenna-pairs separated by nanometer-sized gaps (so called dimers) provide even higher near-field enhancements due to the near-field coupling between the individual components. Thus, higher IR signal enhancements in nanoantenna-assisted SEIRS are expected for dimers, since the signal enhancement scales with the electromagnetic near-fields [5]. In preliminary nanoantenna-assisted SEIRS studies using nanoantennas arranged in lines and separated by gaps with non-uniform gap sizes between 20 and 30 nm we observed this expected increase in IR signal enhancement [6]. At that time a reproducible and uniform fabrication of nanogaps was not achieved. Such a preparation is especially demanding in the case of nanoantenna-assisted SEIRS, as structures with micrometer length have to be fabricated with gaps in the 20-nm regime. However, in contrast to that earlier work, we now successfully prepared gaps down to 10 nm with special electron beam lithography (EBL) techniques in a reproducible manner and performed nanoantenna-assisted SEIRS on dimers instead of lines to exclude any kind of far-field coupling, which may also influence the IR signal enhancement under special conditions, e.g. [7].

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2. Sample preparation

Gold nanoantenna-dimers arraged in arrays with distances large enough to avoid far-field interaction were fabricated by EBL on CaF_2 substrates (see Fig. 1a). The gap g_x between the two antenna arms is varied stepwise from 5 000 nm (no interaction) down to 10 nm (strongly interacting).

The dimers were covered with a monolayer of deuterated octadecanethiol (d-ODT) to probe the near-fields and to estimate an IR signal enhancement in dependence of the gap size g_x. In contrast to biological relevant proteins, d-ODT features a rather simple chemical structure and thus a much simpler IR spectrum. Additionally, it easily adsorbs on gold due to the particular affinity of sulfur, which inhibits absorption on surfaces others than gold, ensures a defined orientation of the molecules as well as a defined monolayer thickness ($d \approx 2.8$nm). Due to the use of deuterated hydrogen the vibrational bands of d-ODT can be clearly separated from non-deuterated ones (for example CH_2 vibrations) originating from residues of the EBL preparation process.

3. Nanoantenna-assisted SEIRS

Typical relative transmittance spectra (IR transmittance at the position of the nanoantenna dimers divided by the transmittance of the bare CaF_2 substrate) acquired by means of microscopic IR spectroscopy [2] before and after the deposition of one monolayer d-ODT are shown in Fig. 1b).

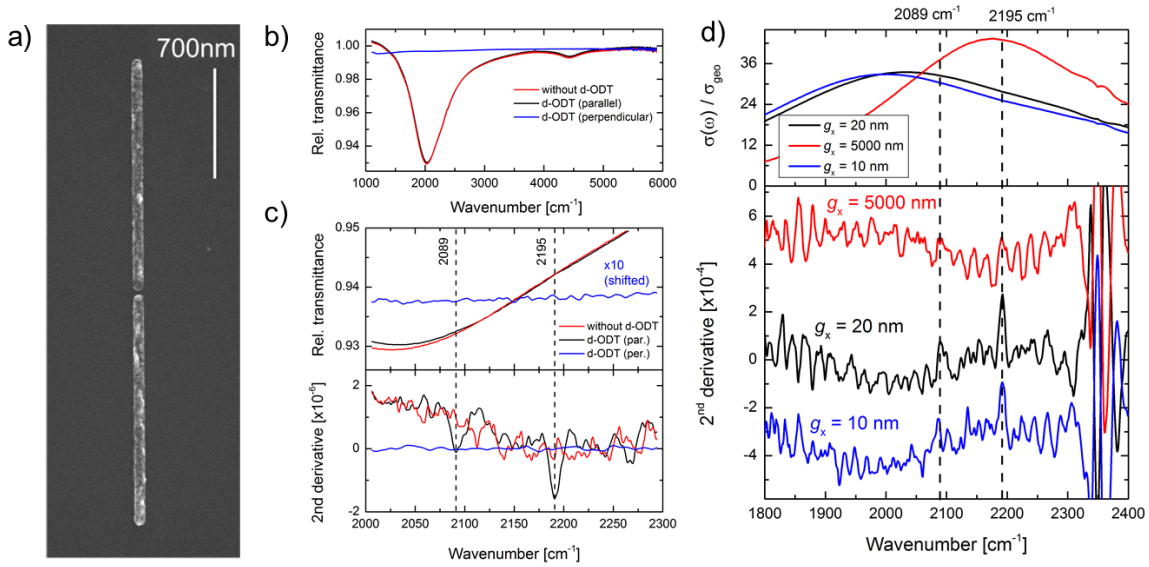

Fig. 1: a) Representative SEM image of a nanoantenna-dimer with length L = 1420 nm, height h = 60 nm, width w = 60 nm and gap g_x = 20 nm. b) Typical polarization depended relative transmittance spectra of a nanoantenna-dimer with L = 1300 nm, $w = h$ = 60 nm and g_x = 20 nm. c) Upper panel: zoom of figure b) and smoothened (Savitzky-Golay, 25 points) second derivative (lower panel). d) Upper panel: far-field extinction cross-section σ(ω) (normalized to the geometric one σ_{geo}) of dimers with fixed lengths (L = 1300nm) and widths ($w = h$ = 60 nm) in dependence of the gap size g_x as given in the legend. Lower panel: Second derivative of the extinction cross-section (shifted for reasons of clarity), which makes the Fano-type vibrational features on the huge antenna background visible. The dashed lines indicate the symmetric and asymmetric CD_2 stretching vibrations of d-ODT as obtained from IR reflection absorption spectroscopy.

A shift of the resonance frequency induced by the change of polarizibility of the surrounding medium (basic principle of a classical localized plasmon resonance sensor, e.g. [8]) is not observed, since the polariziblity is rather small and only a thin d-ODT layer is added around the nanoantennas. The enhanced IR vibrational modes of d-ODT cannot be seen directly in the transmittance spectrum (Fig.1c) upper panel). To make them visible, we calculate the second derivative of the relative transmittance, which is very sensitive to narrow-band changes on a broadband background. As a result we obtain the curves in Fig.1c) showing the enhanced d-ODT signals at 2089 cm^{-1} and 2195 cm^{-1} for illumination with parallel (parallel to the long antenna axis) polarized IR radiation. Neither for perpendic-

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ular polarization (blue curve in Fig.1c) nor in the spectrum without d-ODT (red curve in Fig. 1c) vibrational bands are found, which verifies the SEIRS activity.

The impact of different gaps and thus different near-field enhancements on the IR signal enhancement in SEIRS is shown in Fig.1d). To ensure comparability with respect to the enhanced IR signals of d-ODT, we calculate the extinction cross-section related to the geometric cross-section (Fig. 1d), upper panel) as described by [2]. In accordance with visible (e.g. [8]) and IR (e.g. [9]) spectroscopic studies of coupled nanoantennas, we observe a resonance shift of strongly interacting nanoantennas towards lower energies in comparison to non-interacting ones (see Fig. 1d, upper panel). Since the strongest IR signal enhancement is expected to appear close to the resonance frequency, the antenna, which is tuned best, should feature the strongest signal enhancement in absence of near-field coupling effects. Compared to the plasmonic antenna resonance, the enhanced vibrational bands are too small to show up on the same extinction scale. Zoom in is needed, but even better, calculating the second derivatives makes the vibrational features visible without artificial background subtraction (see Fig. 1d, lower panel). As a result, enhanced signals of d-ODT are found for dimers whereas no enhanced signal is observed above the noise level for individual nanoantennas in spite of their resonance better matches the d-ODT vibrational bands. This behaviour clearly demonstrates the additional IR signal enhancement originating from increased near-fields of interacting nanoantennas, even if a detailed analysis of the IR signal enhancement was hampered by the rather low signal to noise ratio.

4. Conclusion

In summary, we successfully prepared dimers featuring 10-nm gaps for nanoantenna-assisted SEIRS and experimentally demonstrated the increased IR signal enhancement due to inter-particle near-field coupling. Our results indicate the way to ultra-sensitive nanoantenna-assisted SEIRS employing nano-sized gaps which may be further reduced by photochemical metal deposition [10] to take advantage of even higher enhancements for stronger coupled dimers.

Acknowledgments

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