Supplementary Materials

Plasmonic Gold Nanohole Arrays for Surface- Enhanced Sum Frequency Generation Detection

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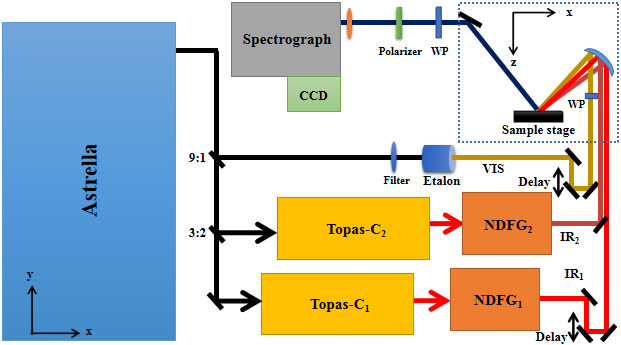
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SFG and Surface-Enhanced SFG (SE-SFG)

SFG is a second-order nonlinear spectroscopic technique. When the incident laser beams VIS and IR are spatially and temporally overlapped on the sample surface, the SFG signal = + radiates at the phase matching direction (= + ). SFG is surface/interface selective under dipolar approximation. Through SFG spectroscopy, surface molecular structure, orientation, packing, and dynamics (ultrashort pulses used in SFG) may be explored. The theory of SFG has been profoundly expounded in Ref [1-3]. If the electric field of incident and/or output radiation is coupled to the LSPR/SPP of interfacial materials, the SFG signal will be enhanced, namely surface-enhanced SFG (SE-SFG) which can be realized similarly as SERS. There are few major aspects worth mentioning in SE-SFG: (1) SFG is a coherent optical process, the role of two incident beams need to investigate; (2) ultrashort laser pulse has much higher energy flux than a continuum laser source, which may induce extra nonlinear effects; (3) photo-induced damping will increase electron-electron scattering, and reduce the dephasing time and EF. Lis *et al.* have reviewed the application of SE-SFG in the plasmonic nanomaterials [3]. Recently, Busson *et al* summarized SE-SFG [4] and significant role of hotspot in SE-SFG [5]. He *et al.* did pioneering research on Shell-Isolated-Nanoparticle-Enhanced SFG (SHINE-SFG) and proposed a new mechanism of SE-SFG, i.e., the nonlinear coupling of SHINE-SFG with difference frequency generation (DFG) [6].

SFG experimental setup



**Figure S1.** Schematic of broadband SFG (BB-SFG) experimental setup.

The SFG measurements were performed in reflection geometry as shown in Figure S1. The light sources were generated with a 35 fs amplifier (Astrella, Coherent), 6 mJ/pulse, centered at 800 nm at 1 kHz repetition rate. A small portion of the amplifier output (10%) was passed through a narrowband filter (808 nm, 3 nm FWHM, Semrock) and an Etalon (800 nm, 1 nm FWHM, SLS Optics Ltd.) to generate the VIS beam. The rest of the amplifier output was used to generate the IR with commercial optical parametric amplifier (TOPAS, Light Conversion) and non-colinear difference-frequency generation (NDFG). As illustrated in Figure S1, the VIS and IR beams are in the same plane with incident angles of 57°, 63° respect to the surface normal, and were focused on the sample with the spot diameter of 260 μm and 500 μm, respectively. The incident energies of the IR and VIS at the sample were 5 μJ/pulse and 1 μJ/pulse if not otherwise specified.

**FWHM values of the SPP modes**

The reflectance value at the dip is denoted with R1, and that at the left/right shoulder is denoted with R2. The FWHM of the SPP mode is then taken at the reflectance value of (R1 + R2)/2, as indicated with the double-arrow line in Figure S2 [7]. The calculated FWHM values and the dip positions of the SPP modes are summarized in Table S1.



**Figure S2.** Determination of the FWHM value of the SPP modes.

**Table S1.** Dip positions and FWHM values of the SPP modes of the Au NHAs.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| **incident angle**  **/ °** | **Mode 1**  **/ nm** | **FWHM 1**  **/ nm** | **Mode 2**  **/ nm** | **FWHM 2**  **/ nm** | **Mode 3**  **/ nm** | **FWHM 3**  **/ nm** |
| 7.9 | 663.5 | -- | -- | -- | 682.9 | -- |
| 12.4 | 692.9 | 22.0 | -- | -- | 692.5 | -- |
| 16.9 | 722.1 | 24.4 | 708.4 | -- | 708.4 | 62.2 |
| 21.4 | 753.2 | 25.4 | 727.7 | -- | 727.7 | 62.4 |
| 25.9 | 785.2 | 25.4 | 753.9 | -- | 743.4 | 71.9 |
| 30.4 | 814.4 | 21.9 | 789.1 | 14.0 | 750.4 | 79.0 |
| 34.9 | 842.8 | 20.2 | 815.4 | 13.1 | 757.5 | 64.8 |
| 39.4 | 870.3 | 16.7 | 842.6 | 20.2 | 754.0 | 45.6 |
| 43.9 | 896.0 | 16.6 | 861.9 | 14.1 | 786.4 | 43.8 |
| 48.4 | 919.8 | 15.7 | 882.0 | 12.2 | 798.7 | 42.1 |
| 52.9 | 941.3 | 13.9 | 897.7 | 14.1 | 805.7 | 54.3 |
| 57.4 | 961.6 | 12.5 | 913.6 | 14.1 | 812.8 | 52.8 |
| 61.9 | -- | -- | 927.6 | 14.0 | 823.2 | 50.8 |
| 66.4 | -- | -- | 938.1 | 12.4 | 828.5 | 40.2 |

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