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Nonlinear Nanophotonic Systems for Harmonic Generation, Parametric Amplification, Optical Processing and Single-Molecule Detection

by

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ABSTRACT

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Metallic nanoparticles support collective oscillations of conduction-band electrons, in response to light incidences. Such phenomenon is called localized surface plasmons, which confine large electromagnetic fields in sub-wavelength dimensions, enabling the light manipulation at the nanoscale. Plasmonic nanoparticles have established many promising applications, such as infrared photodetections, photothermal generation steam, chemical photocatalysis, cancer therapy and surface-enhanced spectroscopy. More interesting, plasmonic nanostructures could generate strong nonlinear-optical effects by relatively low excitation powers, and have been widely used in different processes like second-harmonic generations (SHG), difference-frequency generation (DFG), third-harmonic generation (THG), optical four-wave mixing (FWM) and surface-enhanced Raman scattering (SERS).

This thesis will focused on two types of second-order and two types of third-order nonlinear-optical processes, enhanced by artificial plasmonic nanostructures. Firstly, the second-harmonic generation on a single nanocup is studied, and the signal is demonstrated to have increasing intensity as the 3D symmetry of the
nano
cup is reduced. Then, optical four-wave mixing is generated on a plasmonic nanocluster which supports a coherent oscillation of two Fano resonances. The electric fields from both Fano resonances add coherently resulting in strong fields and correspondingly large signals. This nanocluster has a large color-conversion efficiency, and could be used for building blocks of optical processors that convert two input colors into a third color. Later, one specific application of four-wave mixing, the coherent anti-Stokes Raman scattering (CARS) is studied. By exploiting the unique light harvesting properties of a Fano resonance of a specially designed nano-quadrumer, the surface-enhanced CARS (SECARS) technique amplifies the Raman signals of molecules on the quadrumer by about 100 billion times. This enables the accurate identification of a single molecule with less than 20 atoms. Finally, a plasmon-enhanced optical parametric amplifier (OPA) is designed: A BaTiO$_3$ nanosphere is used as the nonlinear OPA medium; A nanoshell wrapping this nanosphere is used as a triply resonant cavity for all the pump, signal and idler beams; The generated idler beam has a wide tuning range in the near-infrared and also adjustable bandwidth. This surface-plasmon-enhanced OPA (SPOPA) could be an efficient light source working in the infrared regime, with large wavelength tunabilities and nanoscale dimensions easily integrated into the next-generation optoelectronic devices.
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# Nomenclature

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<th>Description</th>
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<td>SHG</td>
<td>Second-harmonic Generation</td>
</tr>
<tr>
<td>FWM</td>
<td>Four-wave Mixing</td>
</tr>
<tr>
<td>SECARS</td>
<td>Surface-enhanced Coherent Anti-Stokes Raman Scattering</td>
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<tr>
<td>SERS</td>
<td>Surface-enhanced Raman Scattering</td>
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<tr>
<td>OPA</td>
<td>Optical Parametric Amplification</td>
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Chapter 1

Introduction

The field of plasmonics, an important part of nanophotonics, has attracted great attentions and demonstrated various applications in the recent decade. In present of some external incidence, metallic nanoparticles have collective oscillations of the conduction-band electrons (known as plasmons) and support localized plasmon resonances. These resonances can be tuned from UV to mid-infrared frequencies depending on the geometry, dimension and embedded medium of the nanoparticles. Plasmon resonances generate large local electromagnetic fields, where the nanoparticles efficiently couple and confine light enabling the light manipulation and exhibiting unique optical properties. One such new optical phenomenon is Fano resonance, usually generated by sophisticated nanostructures (made of several constituents), have been shown to support extremely large local fields as a result of coupling between broad superradiant and narrow subradiant modes.
Plasmonic nanoparticles enabled lots of optically-driven applications such as environment sensing\textsuperscript{1}, infrared photodetection\textsuperscript{2,3}, solar energy harvesting\textsuperscript{4,5}, chemical photocatalysis\textsuperscript{6,7}, cancer therapy\textsuperscript{8-10} and surface-enhanced molecule sensing\textsuperscript{11-13}. Especially interesting, when the fields are enhanced and confined in a small volume, strong nonlinear optical effects could be generated by relatively low excitation powers\textsuperscript{14}. This nonlinear plasmonic response is usually several orders of magnitude larger than that of nonresonant dielectric media\textsuperscript{15,16}, and has been used to enhance different nonlinear optical processes as second-harmonic generations (SHG)\textsuperscript{17-19}, third-harmonic generation (THG)\textsuperscript{20-22}, four-wave mixing (FWM)\textsuperscript{15,23,24} and surface-enhanced spectroscopies\textsuperscript{25,26}. Several different types of nonlinear optical responses enhanced by artificial plasmonic nanostructures will be the focus of this thesis.

Chapter 2 consists of some background information applied throughout the thesis. It begins with some fundamental concepts of plasmons, including the Maxwell's equations used in solving the optical (electromagnetic) responses of subwavelength-size nanoparticles, the complex dielectric function describing the material's dissipation and dispersion, surface plasmon polaritons and localized surface plasmons, and various theoretical modeling methods. Later a nanocup, as a symmetry breaking of a nanoshell, is introduced for its unique light-bending property. Then the origin and underlying physics of a Fano resonance in a plasmonic nanostructure is explained. Then the surface-enhance Raman scattering (SERS) spectroscopy is described for the amplification of the weak spontaneous Raman
scattering. Lastly, the physics of nonlinear optics and various nonlinear optical processes are discussed.

Chapter 3 depicts one type of second-order nonlinearity, the second-harmonic generation on a single nanocup. The fabrication and substrate-transfer techniques for nanocups are designed, and the specific light-bending property of the nanocup magnetic mode is investigated using a specially designed dark-field microscope. The second-harmonic generation is demonstrated to have increasing intensity as the 3D symmetry of the nanocup is reduced. With efficiencies similar to commercial SHG crystals, nanocups provide a promising approach for the design and fabrication of synthetic second-order nonlinear optical materials.

Chapter 4 shows one type of third-order nonlinearity, the optical four-wave mixing on a plasmonic nanocluster. This nanocluster supports a coherent oscillation of two Fano resonances within the same structure, where the electric fields from the two modes add coherently resulting in strong field enhancements. In comparison, other double-resonant plasmonic clusters lacking coherence give rise to lower four-wave mixing efficiencies. With a much higher color-conversion efficiency relative to existing nonlinear optical materials, this coherent double-resonant nanocluster offers a new strategy for designing high-performance third-order nonlinear optical devices, such as an optical processor that can mix two different colored light beams to produce a third, entirely different colored beam.

Chapter 5 builds upon chapter 4. It demonstrates one specific application of the optical four-wave mixing: the coherent anti-Stokes Raman scattering (CARS)
enhanced by a plasmonic quadrumer. By exploiting the unique light harvesting properties of a Fano resonance in this quadrumer, the surface-enhanced CARS technique amplifies the optical signature of molecules by about 100 billion times. This enables the accurate identification of a single small molecule (containing around 20 atoms), which is verified by a statistically rigorous bi-analyte method. This approach combines single-molecule spectral sensitivity with simple lithographic substrates, and could have tremendous applicability in fields as diverse as medical diagnostics, forensics, and homeland security.
2.1. Plasmon

Plasmon is the collective oscillations of free electrons in the metallic structures, in response to the external electromagnetic (EM) fields, thus it is a quantum of plasma oscillation. It forms a major part of nanophotonics, which explores the EM fields confined over dimensions similar or smaller than the wavelength\(^2\). Plasmon oscillations have large amplitudes when they are on resonances, usually at optical frequencies, where the plasmonic structures efficiently couple and confine light enabling the light manipulation at the nanoscale.

2.1.1. Maxwell’s equations and dielectric functions

Plasmonic metals can be treated as incompressible, irrotational liquid of electrons (negatively charged) sitting on a fixed background of atomic lattice (positively charged). Although plasmon oscillation is a type of quantum phenomena,
the high density of electrons results in small spacing of the electron energy levels compared to thermal excitations of energy \( k_B T \) at room temperature, thus there is no need to use quantum mechanics\(^2\). We can study the interaction between the external EM fields and the plasmonic nanostructures by a classical model with Maxwell’s equations\(^2\):

\[
\begin{align*}
\nabla \cdot \mathbf{D} &= \rho_f \\
\nabla \cdot \mathbf{B} &= 0 \\
\nabla \times \mathbf{E} &= -\frac{\partial \mathbf{B}}{\partial t} \\
\nabla \times \mathbf{H} &= \mathbf{J}_f + \frac{\partial \mathbf{D}}{\partial t} \\
\mathbf{D} &= \varepsilon \varepsilon_0 \mathbf{E} \\
\mathbf{B} &= \mu \mu_0 \mathbf{H}.
\end{align*}
\]

Here \( \rho_f \) is the free charge density, \( \mathbf{J}_f \) is the free current density; \( \varepsilon_0 \) and \( \mu_0 \) are the permittivity (dielectric function) and permeability of vacuum, respectively; \( \varepsilon \) and \( \mu \) are those of the metal.

The dissipative and dispersive characteristics of the EM waves in the material can be described by a complex dielectric function \( \varepsilon(\omega) = \varepsilon'(\omega) + \varepsilon''(\omega) \), where \( \varepsilon'(\omega) \) (real part) mainly determines the phase velocity of EM waves due to the material polarization, and \( \varepsilon''(\omega) \) (imaginary part) determines the amount of energy loss due to absorption (damping). Plasmon decays via different damping
pathways²⁹: 1. radiative damping: plasmon excites photons, 2. Non-radiative damping: intra-band transitions within the conduction band, and inter-band transitions due to within d-bands (in noble metals) and the conduction band, 3. electron-electron scattering or electron-phonon scattering.

For noble metals such as gold and silver, inter-band transitions lead to strong absorption at ultraviolet frequencies. For aluminum, inter-band transitions are at ~ 1.5 eV (Near-infrared)³⁰. By using Maxwell’s equations with suitably selected dielectric functions for all metals, such as the Johnson and Christy’s dielectric functions³¹, the optical responses of plasmonic structures can be easily calculated. This approach does not need detailed study of the interactions between charged particles in media and applied EM fields, since the rapidly varying fields are averaged over distances much larger than the underlying nanostructures²⁷. On the contrary, the dielectric functions obtained by a free electron gas model (Drude model³² for the optical response of metals) haven’t take into consideration of the inter-band transitions, thus break down in the corresponding regions of visible or ultraviolet.

2.1.2. Surface plasmon polaritons and localized surface plasmons

Surface plasmon polaritons (SPP) are 2-dimensional EM waves travelling along the conductor-dielectric interface, evanescently confined in the perpendicular direction²⁷, and damped due to energy loss to the metal absorption or scattering into other directions. SPP can be excited on metal films, insulator/metal/insulator (IMI) or metal/insulator/metal (MIM) sandwiches³³, prisms³⁴,³⁵, gratings³⁶,³⁷,
highly-focused laser beams\textsuperscript{38}, near-field fiber tips\textsuperscript{39} or nanowires\textsuperscript{40,41}. SPPs demonstrate great potentials such as the controlling of light propagation in matter\textsuperscript{42,43}, strong field-enhancements for nonlinear materials\textsuperscript{44}, and quantum information transmission\textsuperscript{45,46}.

More commonly studied are the localized surface plasmons (LSP), which are non-propagating excitations of conduction-band electrons in the metallic nanoparticles. When the nanoparticles are on resonant with the applied EM fields, they can generate and confine significantly enhanced fields in the particle near-fields. These structures have a wide range of applications such as environment sensing\textsuperscript{1}, infrared photodetection\textsuperscript{2,3}, solar energy harvesting\textsuperscript{4,5}, chemical photocatalysis\textsuperscript{6,7}, cancer therapy\textsuperscript{8-10}, surface-enhanced molecule sensing\textsuperscript{11-13} and building blocks for metamaterials\textsuperscript{47-50}.

2.1.3. Theoretical modeling

The interaction between a metallic nanoparticle and the external EM wave gives rise to localized surface plasmon resonances (LSPR) at some specific wavelengths. These resonances have important optical properties such as the particle's extinction (sum of absorption and scattering) usually get maximum values at the resonant frequencies, and the particle's near-fields can be greatly enhanced. These specific properties of LSPR require the specific design of functional plasmonic nanostructures, where different theoretical modeling techniques are needed.
In 1908, Gustav Mie\textsuperscript{51} developed a complete theory of the scattering and absorption of EM waves by a sphere, now known as Mie theory\textsuperscript{52} to study the LSPR of spherical nanoparticles by solving Maxwell’s equations. However, Mie theory is limited to the rare situations of spherically symmetric particles, while more complex structures are necessary nowadays with a variety of different shapes, sizes, or ensembles of particles, for purposes of their unique optical properties.

Recently, a new modeling method called plasmon hybridization method\textsuperscript{53,54} has been invented. As an EM analog of molecular orbital theory, the Langrangian for a complex structure (consisting of several simpler elementary structures) can be expressed by the plasmon oscillation amplitudes of elementary structures with an interaction term that describes the coupling between the elements. Therefore, plasmon hybridization method provides a qualitative and quantitative understanding of the underlying physics of complex structures, by simplifying a complex structure into hybridization of their elementary structures.

More general modeling methods could be the numerical simulation methods, which are applicable to almost all arbitrarily geometries, although there may be very little understanding of the underlying physics. These techniques include Finite Element method (FEM)\textsuperscript{55} and the Finite-difference-time-domain (FDTD)\textsuperscript{56} method, both based on solving differential Maxwell’s equations on a set of discrete subdomains. The latter covers a wide frequency range with a single simulation run, since it is a time-domain method. Nowadays commercial software is available for both techniques, such as COMSOL for FEM and Lumerical for FDTD. The numerical
methods are usually limited by the computer capability and amount of time consumed.

2.2. Nanoshell and nanocup

Nanoshells are symmetric spherical nanoparticles consisting of a dielectric core (usually SiO₂) covered by a thin metallic shell (usually gold). They are made by wet chemical synthesis⁵⁷,⁵⁸, where the SiO₂ core (commercial available or grown by the standard Stöber process⁵⁹) is functionalized by aminopropyltriethoxysilane (APTES) first to attach small Au beads (1-2 nm), and then a complete Au layer was formed by reduction of additional gold salt solution (HAuCl₄).

![Figure 2.1](image)

**Figure 2.1** (a) Schematic geometry of an Au/SiO₂ nanoshell. (b) Tunable plasmon resonance of a nanoshell with a 120-nm-diameter SiO₂ core and varying thicknesses of Au shell.

Gold nanoshell has big advantages, since it is a simple structure with its LSPR wavelength easily tunable from visible to mid-infrared by varying the ratio of
core/shell dimensions (Figure 2.1, from the reference\textsuperscript{60}). Another interesting feature of the nanoshell is the intense near field, with various applications such as photothermal cancer treatment\textsuperscript{10,61}, surface enhanced Raman scattering\textsuperscript{62,63}, photodetector\textsuperscript{64} and nonlinear optics\textsuperscript{65,66}.

**Figure 2.2** Different reported fabrication procedures for nanocups. The top route (red arrows) is based on chemical synthesis of nanoshells followed by etch procedures; the bottom two routes (blue arrows) deal with templated deposition processes on top of immobilized dielectric beads.

By breaking the symmetry of originally symmetric nanoshells, one obtains semishells, also known as nanocups. Nanocups are metallodielectric “Janus” nanoparticles\textsuperscript{67}, consisting of a dielectric (e.g., silica) nanoparticle upon which a hemispherical layer of metal (e.g., Au) is deposited. To date, there are a number of different techniques reported to fabricate nanocups (Figure 2.2, from the reference: Semishells: Versatile Plasmonic Nanoparticles). Nanocups are a particularly promising 3D nanostructure with reduced-symmetry (additional degrees of
freedom), for the development of metamaterials and novel optical media\textsuperscript{68-70}. The resonances of nanocups depend on the sizes of the spherical dielectric core and the hemispherical metallic layer, and most specifically on their orientation with respect to incident light. Nanocups have been shown to possess magnetic dipole modes that redirect incident light along its axis of symmetry, a unique light-scattering property that makes it the nanoscale analog of a parabolic antenna (Figure 2.3, from the reference\textsuperscript{71}). They are an important member of a growing class of subwavelength optical components with unusual, even counterintuitive, optical light-scattering characteristics\textsuperscript{72-74}.

**Figure 2.3** Nanocup plasmon modes and calculated far field angular scattering (red patterns) for different nanocup orientations relative to the incidences. (a) Higher-energy electric mode with no light redirection. (b) Lower-energy magnetic mode with directional scattering along the nanocup’s axis of symmetry.
2.3. Fano resonances in plasmonic nanostructures

In 1961, an Italian physicist Ugo Fano gave a theoretical explanation for the distinctly asymmetric lineshape of inelastic scattering of helium electrons\(^{75}\), which bears his name. In the theory of Fano resonance (FR), the asymmetric lineshape is coming from the interference between a scattering within a continuum of states (the background) and another scattering due to a discrete excited state (the resonance). The energy of the resonant state must lie in the energy range of the continuum (background) states for the effect to occur. Nowadays, the concept of FR has been widely used for asymmetric lineshape features (due to interference of a broad continuum and a narrow resonance) in many different physics disciplines, such as atomic physics, nuclear physics, condensed matter physics and nonlinear optics.

Over the last decade, FRs have been observed on many plasmonic nanostructures, such as a ring/disk cavity\(^{76}\), a dolmen structure\(^{77}\), a multilayered nanoshell\(^{78}\), an asymmetric split ring array\(^{79}\) and nanoclusters\(^{13,80,81}\). In these structures, a broad-band resonance (superradiant mode) and a narrow-band discrete resonance (subradiant mode) overlap in energy with the each other. The destructive interference (energy exchange) between these two modes gives rise to a prominent Fano “dip” (subradiant) in the otherwise superradiant scattering continuum, through the near-field coupling. The energy overlapping can be achieved by independently tuning the geometries and/or the dimensions of the structural components. The most promising applications of FRs are the chemical and biological...
sensing, due to their great field-enhancements at the Fano “dip” frequencies and high sensitivity to the local dielectric environment.

Figure 2.4 (from the references82,83) shows the origin of the FRs, which comes from the subradiant-superradiant energy exchange. The excitation of the superradiant mode can occur by two pathways with degenerate energies: In pathway I, a photon directly excites the superradiant mode. In path II, a photon excites the superradiant mode, then the energy is transferred to the subradiant mode, then back to the superradiant mode again. Note that there is a phase shift $\pi$ during the energy transfer process in the pathway II (because the coupling occurs at the resonances and is dispersive84), thus there is a $\pi$ phase difference between these two pathways. The corresponding destructive interference between two pathways cancels the polarization of the superradiant mode, and leads to a prominent Fano “dip” (a narrow transparency window) on the superradiant scattering continuum.

**Figure 2.4** Energy diagram of the subradiant and superradiant modes and the generation of a Fano resonance through coupling between these two modes. Pathways 1 represents the direct excitation of the superradiant mode; Pathway 2 represents the indirect excitation of the subradiant mode through the superradiant mode. Widths of the bars in the vertical direction represent the linewidths of the modes.
2.4. Surface-enhanced Raman scattering

In 1928, Sir Chandrasekhra Venkata Raman and Grigory Landsberg independently discovered the inelastic scattering of a photon from a molecule in liquids\textsuperscript{85} and crystals\textsuperscript{86}, respectively. This process is first referred to as the “Smekal-Raman effect” in 1931 and simply “Raman effect” later. This ground-breaking work earned C. V. Raman the Nobel Prize for Physics in 1930.

In general, when light strikes a molecule (or an atom), there are two types of scattering processes (see Figure 2.5): 1. The majority of photons bounce off such that the scattered photons have the same energy as the incident photons. This elastic scattering is referred to as Rayleigh scattering. In this process, the molecule is first excited to a virtual state and then immediately relax back to its initial state. 2. A small portion of the incident photons are absorbed and re-emitted (scattered) by a molecule, leaving the molecule in another vibrational state that differs from its initial state. The scattered photons thus have a frequency different from the incident photons, and this inelastic scattering is referred to as Raman scattering. Other than these two processes, some of the incident photons may directly pass through the molecules.
Figure 2.5 Energy diagram of different scattering processes.

The inelastic Raman scattering have two possible outcomes: 1. The Stokes Raman scattering: The molecule starts from the ground state and ends up in an excited vibrational state, where the molecule gains energy and the re-emitted photon has a lower energy than the absorbed photon. 2. The anti-Stokes Raman scattering: The molecule starts from an excited vibrational state ground state and ends up in the ground state, where the molecule loses energy and the re-emitted photon has a higher energy than the absorbed photon. In both situations, the difference in energy between the absorbed photons ($\omega_P$) and re-emitted photons ($\omega_S$) equals to the vibrational energy ($|\omega_P - \omega_S|$) of the molecule; each Stokes scattering process has a corresponding anti-Stokes scattering process between the same upper and lower vibrational states, thus belong to the same vibrational mode.

Different molecules have unique information of their molecular structures like the mass of atom, the strength of the bond, the conformation, as well as the specific molecular arrangements. The atoms of a molecule can compress or stretch...
along a bond axes, or can bend symmetrically or asymmetrically. These different vibrational modes occur at unique frequencies, and can be measured based on the re-emitted photons through the Raman spectroscopy. Scientists can further decipher the types of atoms in a molecule as well as their structural arrangement. Thus, Raman spectroscopy provides “fingerprint” of any molecules in the gas, liquid, or solid phases.

However, Raman scattering is inherently a very weak process: For different Raman modes of most molecules, the differential cross-sections\(^{88}\) are usually on the order of \(10^{-31} \sim 10^{-26}\) cm\(^2\). When compared with the real cross-section of a molecule (usually larger than \(10^{-14}\) cm\(^2\)), we find that less than one in one trillion photons will undergo a Stokes or anti-Stokes Raman scattering process. It turns out that a technique to greatly enhance the Raman scattering efficiency is in need.

Surface-enhanced Raman scattering (SERS) is a surface-sensitive technique that significantly enhances the Raman scattering signals of molecules adsorbed on surfaces of rough metal films or plasmonic nanostructures. The SERS effect was first observed from pyridine on a rough silver electrode by Martin Fleischmann et al. in 1974\(^{89}\). To explain the SERS mechanism, Richard P. van Duyne proposed an electromagnetic (EM) theory\(^{90}\): a pump laser on resonance with a plasmonic nanostructure will excite the LSPR and amplify the local field at the pump frequency \(\omega_P\). The re-emitted photons will also experience an amplified local field at the scattering frequency \(\omega_S\). Since at both stages of absorption and re-emission the local
fields are enhanced, the overall electromagnetic enhancement factor in SERS is given by

\[ G_{\text{SERS}} = \left| \frac{E(\omega_P)}{E_0(\omega_P)} \right|^2 \left| \frac{E(\omega_S)}{E_0(\omega_S)} \right|^2. \]  

(2.7)

At the meantime, Albrecht and Creighton proposed a charge-transfer (CT) theory\(^9\): Electrons can either transfer from the Fermi level \((E_F)\) of the metal to the affinity (LUMO) level of adsorbed molecules and then returns back to the metal with molecules remain vibrationally excited, or transfer from the affinity (HOMO) level of adsorbed molecules to the metal and then returns back. The CT effect may only apply to some specific cases, and the SERS enhancements are generally contributed by both EM and CT mechanisms. SERS enhancement factor on the order of \(~10^8\) is able\(^8\) to detect single-molecules with Raman cross-sections of \(10^{-26}\) cm\(^2\), and SERS enhancement factor as large as \(10^{11}\) should facilitate the detection of single molecules with Raman cross-sections of \(~10^{-29}\) cm\(^2\).

### 2.5. Nonlinear optics

Nonlinear optics (NLO) is a specific area of optics, which studies the “nonlinear” interaction of light with matter. That is, the dielectric polarization \(P\) of the media responds nonlinearly to the electric field \(E\) of the light. At low light intensities, typical non-laser sources, the properties of materials remain independent of the illumination intensity. With very high light intensities (electric field comparable to interatomic electric fields, \(~10^8\) V/m), such as lasers, optical properties of materials can be modified. In this case, light waves can interact and
exchange momentum and energy, and result in the generation of optical fields at new frequencies\textsuperscript{92}: The new frequency generation is thus called nonlinear optics. The first demonstration of nonlinear optics is the observation of second-harmonic generation by Franken at University of Michigan in 1961\textsuperscript{93}.

The nonlinear optics could be classified into different orders of nonlinearity: the second-order nonlinear effects include sum-frequency generation (SFG), second-harmonic generation (SHG), Difference-frequency generation (DFG), optical parametric amplification (OPA) and etc. The third-order nonlinear effects include third-harmonic generation (THG), four-wave mixing (FWM), two-photon absorption (TPA), Raman scattering, optical Kerr effect, self-phase modulation and cross-phase modulation, and etc.

In a parametric process, the light waves interact with the medium, and then leave with the energy and momentum of medium unchanged. The total energy and momentum of the incident waves are thus conserved (energy & momentum conservation), which are called phase-matching conditions and usually polarization dependent. In contrast, a non-parametric process is a process in which energy and/or momentum of the medium have been changed. The first six processes in last paragraph are parametric processes and the last five processes are non-parametric processes.
2.5.1. Polarization and susceptibility

We consider the light-matter interaction, where the polarization \( P \) of a medium (dipole moment per unit volume) depends on the strength of the applied optical field \( E \):

\[
P = \varepsilon_0 \left[ \chi^{(1)} E + \chi^{(2)} E^2 + \chi^{(3)} E^3 + ... \right] = P^{(1)} + P^{(2)} + P^{(3)} + ..., \tag{2.8}
\]

where the polarization \( P \) and electric field \( E \) is related through the susceptibility \( \chi \). \( \chi^{(1)} \) is known as the linear (first-order) optical susceptibility, and \( \chi^{(2)} \) and \( \chi^{(3)} \) are known as the nonlinear (second-order and third-order) susceptibilities. In linear optics, the induced polarization \( P \) depends linearly on the applied field \( E \) and is described by the first (linear) term only in equation (2.8). In nonlinear optics, the optical response could be described by higher-order (nonlinear) terms in equation (2.8).

In a simplified case of isotropic media, the polarization \( P \) is parallel to the electric field \( E \), and all terms of \( \chi \) are scales. For condensed matter \( \chi^{(1)} \) is of the order of unity\(^{94} \). By using the Lorentz model of an atom, which treats the atom as a harmonic oscillator, one can estimate \( \chi^{(2)} \sim 10^{-11} - 10^{-12} \) pm/V and \( \chi^{(3)} \sim 10^{-19} - 10^{-24} \) m\(^2\)/V\(^2\).

For more general case of anisotropic media, the polarization \( P \) and electric field \( E \) are usually not parallel, and equation (2.8) should be written in more general forms of the following: all the susceptibilities should be written in forms of tensors:

\[
P^{(1)}(\omega) = \varepsilon_0 \overrightarrow{\chi^{(1)}}(\omega) \cdot \mathbf{E}(\omega) \tag{2.9}
\]
\[ P^{(2)}(\omega) = \varepsilon_0 \chi^{(2)}(\omega; \omega_i, \omega_j) : E(\omega_i) E(\omega_j) \] (2.10)

\[ P^{(3)}(\omega) = \varepsilon_0 \chi^{(3)}(\omega; \omega_i, \omega_j, \omega_k) : E(\omega_i) E(\omega_j) E(\omega_k) \] (2.11)

Here $\chi^{(1)}$ is a second-rank tensor ($3 \times 3$ matrix, in the $x$-$y$-$z$ Cartesian coordinate system), $\chi^{(2)}$ is a third-rank tensor ($3 \times 3 \times 3$ matrix), $\chi^{(3)}$ is a fourth-rank tensor ($3 \times 3 \times 3 \times 3$ matrix), and so on.

### 2.5.2. Second-order nonlinear effects

The second-order nonlinear optical process is described by the $\chi^{(2)}$ susceptibility, and requires non-centrosymmetry (no inversion symmetry) of the media. Some types of liquids, gases, amorphous solids and crystals display inversion symmetry, thus $\chi^{(2)}$ vanishes for such media and consequently no second-order nonlinear optical processes generated by such media.

**Figure 2.6** Energy diagram for different second-order nonlinear optical processes.
In the sum-frequency generation (SFG), two input laser fields $\omega_1$ and $\omega_2$ generate a frequency at $\omega_3 = \omega_1 + \omega_2$ when they propagate through a non-centrosymmetry medium. In this process, two photons of frequencies $\omega_1$ and $\omega_2$ merge into one photon of frequency $\omega_1 + \omega_2$ (Figure 2.6, left). A specific case is the second-harmonic generation (SHG): It has only one pump frequency $\omega$, and two photons at this frequency generate a signal at the $2\omega$ frequency (Figure 2.6, middle).

For the difference-frequency generation (DFG), one photon at frequency $\omega_1$, stimulated by the presence of a field at frequency $\omega_2$, can be decomposed into two photons: one photon at frequency $\omega_2$ and another photon at $\omega_3 = \omega_1 - \omega_2$ (Figure 2.6, right). If the pump wave ($\omega_1$) is strong enough, a weak signal wave ($\omega_2$) can be amplified and an idler wave ($\omega_3$) can be generated by this process, thus it is known as optical parametric amplification (OPA). This process is of considerable practical significance, since it can give rise to intense coherent radiation in the infrared range\(^9\) where no adequate laser is available, or work as an optical mixer in optical communications, or detect weak light ($\omega_2$) at frequencies where sensitive detectors are not available.

### 2.5.3. Third-order nonlinear effects

The third-order nonlinear optical process can be described by the $\chi^{(3)}$ susceptibility, and is a universal property found in any material regardless of its spatial symmetry (found in both centrosymmetric and non-centrosymmetric media).
Figure 2.7 Energy diagram for different third-order nonlinear optical processes.

One general type of third-order nonlinearity is the four-wave mixing (FWM): three laser fields with frequencies $\omega_1$, $\omega_2$, and $\omega_3$ generate the fourth field at frequency $\omega_{\text{FWM}} = \omega_1 \pm \omega_2 \pm \omega_3$. If the frequency difference $\omega_1 - \omega_2$ of two laser fields is tuned to be resonant with a molecule’s Raman mode, the FWM process $\omega_{\text{FWM}} = \omega_1 - \omega_2 + \omega_3 = \omega_{\text{CARS}}$ is referred to as coherent anti-Stokes Raman scattering (CARS). Figure 2.7 (left) shows another FWM process with two input frequencies ($\omega_1$ and $\omega_2$) and the output frequency $\omega_{\text{FWM}} = 2\omega_2 - \omega_1$. One other case is the third harmonic generation (THG): all three input fields have the same frequency $\omega$ (only one laser source, for example), and three photons at frequency $\omega$ are destroyed creating a single photon at frequency $\omega_{\text{FWM}} = 3\omega$ (Figure 2.7, right).
A metal-capped hemispherical nanoparticle, also known as a nanocup, is an asymmetric plasmonic nanoparticle with electric and magnetic plasmon modes: the latter scatters light in a direction controlled by nanoparticle orientation, making it the nanoscale analog of a parabolic antenna. A nanocup also enables the generation of large electromagnetic fields confined to small volumes, potentially providing a route for the development of nanoengineered nonlinear optics, such as second harmonic generation (SHG). The SHG has increasing intensity as the angle between the incident fundamental beam and the nanocup axis is increased. With conversion efficiencies similar to inorganic SHG crystals, nanocups provide a promising approach for the design and fabrication of stable, synthetic second-order nonlinear optical materials tailored for specific wavelengths.
3.1. Introduction

Advances in nanoparticle synthesis and nanostructure fabrication have resulted in a rapidly expanding variety of nanoscale architectures of increasing complexity. A major motivation for the creation of new nanostructures is the development of optical media with subwavelength optical components as "building blocks": infrared and optical frequency metamaterials are a prime example of this approach. An important criterion for subwavelength optical components is that they couple strongly to either the electric and magnetic field components of incident light, ultimately resulting in new optical media, such as metamaterials, with an optical frequency magnetic response or a negative refractive index in a specific frequency range of interest. Potential applications of metamaterials range from optimized light-coupling into detectors or solar cells, ultrasensitive chemical sensing and electromagnetic cloaking materials.

Nanoscale metamaterial components typically have a strongly polarization-dependent response that requires precise control of their orientation relative to incident light. In most cases, the constituents of metamaterials are planar single-layer or stacked multilayer structures. Less explored are metamaterials consisting of three-dimensional subwavelength components, which present critical fabrication challenges. However, 3D metamaterial components will allow new properties not easily captured by planar designs.

Nanocups, as introduced in the sub-chapter 2.2, is a 3D plasmonic metamaterial. With resonant illumination, the collective oscillation of conduction electrons
generates significantly enhanced EM fields on the nanocup surfaces, enabling strong nonlinear optical effects at relatively low excitation powers\textsuperscript{14}. Second harmonic generation (SHG) is a nonlinear process where two photons are converted into a single photon with twice the energy\textsuperscript{93}, where the intensity of generated light is proportional to the fourth power of the fundamental field amplitude. Therefore a 10-fold enhancement of the incident field, which can be easily realized by metallodielectric nanoparticles like nanocups, will lead to a $10^4$ enhancement of SHG intensity.

In this chapter we demonstrate, the specific light scattering properties of the nanocup magnetic mode are interrogated optically using a specially designed dark field microscope. We establish that the electric and magnetic modes of individual nanocups have significantly different and distinct light-scattering properties. We generate second harmonic UV light from individual, oriented nanocups whose magnetic dipole plasmon resonance is tuned to the incident fundamental. We show that by orienting the nanoparticle with respect to incident light, the observed SHG intensity is greatly increased as the 3D symmetry of the nanostructure is reduced, relative to the symmetrically oriented nanoparticle. Nanoparticle orientation also modifies the emission direction of the second harmonic generated light, which is close to, but not precisely directed along, the nanocup axis of symmetry. With conversion efficiencies much larger than those observed for planar structures and similar to nonlinear crystals in widespread use, this structural motif paves the way for synthetic second-order nonlinear optical materials designed for currently inaccessible wavelengths.
3.2. Orientation-preserved transfer of nanocups

While nanocups can be synthesized by chemical methods, precise nanoparticle morphologies and orientations can be fabricated by depositing the dielectric (silica) core nanoparticles onto a “growth” or “donor” substrate and evaporating a thin gold film onto the nanoparticle-decorated substrate. In this approach, tilting the growth substrate with respect to the metal deposition beam enables the growth of tilted nanocups oriented at the angle of the deposition beam relative to the fabrication substrate. For subsequent use in applications, the nanoparticles need to be removed from this initial substrate and transferred to an “application” or “receiver” substrate, such as an optically transparent film or a semiconductor device, preserving the precise three-dimensional orientation of the nanocups. While a number of useful nanoparticle transfer methods have been reported, we have found that these approaches do not achieve orientation-preserving transfer of these three-dimensional nanostructures.

We designed a method of orientation-preserving transfer of nanocups from their “growth” or “donor” substrate to an “application” or “receiver” substrate, chosen so that the optical properties of the nanoparticles could be studied at the individual nanoparticle level. The new transfer method is based on using an adhesion molecule that will covalently bind to the transferred nanocups and the receiver substrate. Unlike other methods, this enhanced binding preserves the orientation of nanocups after transfer.
Figure 3.1 Schematic illustration of orientation-preserving nanocup transfer:
(1) E-beam deposition of a nanoscale gold layer on silica nanoparticles on a substrate results in a nanocup-nanohole structure. (2) The pre-cured PDMS slab is placed on the donor substrate; (3) PDMS slab is quickly peeled from the initial fabrication substrate, temporarily transferring the nanocups onto the PDMS slab surface; (4) lamination of the nanocups onto the receiver substrate with an intermediate TEOS solution, heated at 110 °C for 10 min then kept in vacuum for 2 days; (5) slow delamination of the PDMS transfer layer uncovers the transferred nanocups on the receiver substrate. SEM images show: (a) nanocups and nanoholes fabricated on the initial substrate, (b) nanocups adsorbed onto the PDMS slab
surface, and (c) empty nanoholes remaining on the donor substrate after PDMS peel-off. The lower resolution of the SEM image (b) arises from the charging of the PDMS substrate.

The procedure for fabricating and transferring nanocups is outlined in Figure 3.1. Nanocups were initially fabricated on a donor substrate by metal evaporation, as previously reported. Briefly, 0.01 wt % aqueous suspension of colloidal silica (50% Colloidal Silica, CPC) were randomly deposited on the surface of a silicon wafer (1 × 2 cm$^2$) previously functionalized with a 1 wt % ethanolic solution of poly(4-vinylphenol) (PVP, Aldrich). A 2 nm thick intermediate Ti layer (promoting adhesion of Au to silica), followed by 30 nm thick Au layer was evaporated onto the substrate by electron-beam evaporation (~ 0.5 Å s$^{-1}$) over the immobilized silica particles, resulting in a thin but continuous Au film coverage on top of the silica nanoparticles (nanocups). In this deposition process, the Au film is also deposited on the donor substrate as well, in the spaces between the nanoparticles, resulting essentially in the fabrication of random nanoholes in the Au film (Step 1). Scanning electron microscopy (SEM, FEI Quanta 400) images of fabricated nanocups and nanoholes produced by this method are shown in Figure 3.1a.

A pre-cured elastomeric polydimethylsiloxane (PDMS, SYLGARD-184, Dow Corning) slab (1 × 1 cm$^2$ and 6 mm thickness) was used as the transfer stamp. After gentle application onto the donor substrate (Figure 3.1, step 2) until the PDMS coated the substrate surface thoroughly, the PDMS slab was quickly peeled off. This transferred the nanocups from the donor substrate onto the stamp (step 3). SEM images of the nanocups attached to the PDMS surface, and the empty nanoholes
remaining on the donor substrate, are shown (Figure 3.1b, c). A nearly 100% transfer yield is achieved in this step, over the range of nanocup sizes fabricated (30 nm to 200 nm). When the PDMS removal is performed rapidly, the (removal rate-dependent) van der Waals force between the nanocups and the hydrophobic PDMS stamp surface is stronger than the initial (rate-independent) binding between the nanocups and the fabrication substrate. Consequently, peeling the PDMS at a high velocity preferentially breaks the adhesion between the silica side of the nanocups and the PVP-functionalized hole “floors” of the growth substrate, transferring the nanocups to the PDMS surface at a high yield. The remaining nanohole-perforated Au film remained unperturbed by this processing step.

A second silicon wafer (1 × 2 cm²) was used as a receiver substrate. It was first treated with an oxygen plasma (660 W; Fischione) for 90 sec to promote an increased density of hydroxyl (-OH) groups on the surface. 4 µL of 2% v/v ethanolic solution (200 proof; Decon Labs) of tetraethyl orthosilicate (TEOS, Si(OCH₃)₄, 99.999%, Aldrich) was added on the substrate. The PDMS slab, which had stripped the nanoparticles from the fabrication substrate, was then placed nanoparticle-side down, carefully, on top of the receiver substrate. The stack was clamped and locked by a 30 mm cage system (ThorLabs) to apply a weak external pressure, which creates a thin layer of TEOS solution between the PDMS and the receiver substrate (step 4). The elastomeric property of PDMS allows an intimate physical contact between the nanoparticles to be transferred and the silicon receiver substrate.
This laminated stack of substrate, TEOS, and nanostructure-PDMS layer was then immediately transferred into an oven (3500 W; Thermo Fisher Scientific) at 110 °C for 10 min. During this step, the ethanol gradually evaporated, promoting the formation of covalent bonds between the oxide surface of the substrate, the TEOS, and the nanocups. This reaction normally proceeds with a certain reversibility. The stack was then placed in a chamber attached to a rotary vane pump (3.3 m$^3$ h$^{-1}$; Edwards) for two days, where a further continuous removal of ethanol drives the formation of a layer of silica in the interface (Figure 3.2). During this lamination procedure, the TEOS bonds the nanocups covalently to the receiver substrate; this covalent interaction is now significantly stronger than the nonspecific interaction between the nanocups and the PDMS stamp. Slow peeling of the PDMS from the silicon wafer released the intact nanocups from the PDMS, leaving them strongly bound to the receiver substrate in the same orientation of placement (step 5). The attraction between the Au layer on the nanocup and the silica nanoparticle core is sufficiently strong to prevent delamination of the nanoparticles themselves.
Figure 3.2 Formation of a TEOS monolayer between nanocups and the substrate surface. Under strict anhydrous conditions, two opposite alkoxy groups of TEOS will selectively react with surface hydroxyl groups of the substrate and nanocups, and a single covalent Si-O-Si-O-Si bond will form at the interface (ethanol condensation). Upon exposure to ambient atmosphere, the two remaining alkoxide groups of TEOS are presumed to be replaced by hydroxyl groups when react with atmospheric water (hydrolysis), and subsequently two neighbor TEOS molecules form siloxane bond (water condensation) which makes the TEOS layer more stable and robust. In contrast, in the present of water moisture, TEOS will be hydrolyzed and subsequently crosspolymerized which competes with the covalent binding of TEOS to the hydroxylated surfaces, and usually leads to the undesirable TEOS colloids.

Figure 3.3 shows a series of SEM images of portions of the receiver substrates with transferred nanocups oriented at (a) 30°, (b) 50°, and (c) 70° with respect to the substrate normal (z-axis). All the transferred nanocups have their cup-opening directing rightward, the same as on the donor substrates. Views of these substrates, tilted at an angle of 75° in the SEM chamber, are shown in the insets in this figure. The areas beneath the nanocups appear dim in these images, due primarily to the
difficulty of secondary electron detection. In all cases, it was found that transferred nanocups kept their orientations with respect to the substrate normal following this process. The angular distribution of the nanocups in the $x$-$z$ plane and the $x$-$y$ plane on each substrate was analyzed (ImageTool, Version 3.00). Nanocup transfer occurred with both high fidelity and high yield, indicating that this technique can be straightforwardly scaled up to a larger surface areas, larger numbers of nanocups, and higher nanocup densities. In additional experiments, it was observed that even smaller nanocups ($\sim 50$ nm) can be transferred with a preserved cup orientation, however, 30 nm nanocups resisted the transfer process at the PDMS stripping step, where the viscosity of PDMS is not enough to peel off the smallest particles, rather than the printing step. By repeating the entire transfer procedure numerous times, an overall transfer efficiency of $\sim 90\%$ was assessed, comparable to other techniques reported for nanoparticle transfer$^{111,114}$. Specific efforts to uniformly hydroxylate the interfacial oxide surfaces of substrate and nanoparticle, and performing the TEOS deposition in a water-free environment such as a nitrogen drybox, may further improve transfer efficiency$^{118,119}$. 
Figure 3.3 Normal and tilted (75°, insets) SEM images of the final substrates showing transferred nanocups with (a) 30°, (b) 50°, and (c) 70° to the z-axis. The histograms evaluate the change of nanocup angles in the x-z (red) and x-y (blue) planes after transfer.
This transfer process can be straightforwardly adapted to position oxide-terminated nanoparticles onto noble or coinage metal substrates, or vice versa, by using mercaptopropyltrimethoxysilane (MPTMS) as the adhesion molecule\textsuperscript{120,121}. Because the transfer process is performed using an elastomer, it could be adapted to the controlled-orientation deposition of nanostructures onto curved, flexible, or unusually shaped surfaces\textsuperscript{107,114}. This process may also be adapted to develop more complex but controlled orientations of reduced-symmetry nanostructures on surfaces, for stepwise-assembled multilayer materials, or for separating a heterogeneous mixture of nanoparticles by laminating each nanoparticle type onto a differently prepared receiver substrate.

### 3.3. Methods and instruments

#### 3.3.1. Custom-built dark-field microscope with variable-angle illumination

We have built a dark-field microscope (Figure 3.4), where white light from a halogen lamp could be directed onto a sample at different angles via a variable-angle illumination arm, which also collimated and polarized the illumination. The scattered light was collected and imaged using a 50× / 0.42 NA microscope objective (M Plan Apo NIR, Mitutoyo) oriented normal to the sample substrate. In this configuration, as long as the angle of incidence of the illumination remains larger than the angle subtended by the 0.42 numerical aperture, only the light scattered by the nanocups will be collected, while the incident light will be reflected in the specular direction, away from the objective lens. The collected light was
imaged using a tube lens (f = 200 mm, MT-L, Mitutoyo), onto the entrance slit of a spectrograph (SP2150, PI/Acton) and detected by a CCD array (Pixis 400, PI/Acton). The raw spectrum of an individual nanocup was then corrected by background subtraction, and the resulting data were divided by the spectrum of a white reflectance standard (Labsphere) to account for the spectral efficiency of the system. In order to locate specific nanocups, the sample was then numerically indexed by evaporating a layer of Ti through a TEM grid (100 mesh Cu micron index 1, Ted Pella) used as a shadow mask.

![Photo of the custom-built dark-field microscope with variable-angle illumination.](image)

**Figure 3.4** Photo of the custom-built dark-field microscope with variable-angle illumination.
3.3.2. Numerical simulation

Optical response of the nanocups were simulated using commercial finite element method (FEM) software (COMSOL Multiphysics 3.5a). The nanocups were modeled as an ellipsoidal semishell, where the back side of the semishell is 30 nm (or 35 nm) thick and tapers to 10 nm (or 20 nm) thick near the rim of the cup. The rim profile was given a 5 nm (or 10 nm) radius of curvature in order to smooth the sharp corners. This geometrical configuration gave the best match to both the SEM and optical data. The metal semishell was modeled using the empirical, bulk dielectric function for Au\(^{31}\), and the silica core was modeled using \( \varepsilon = 2.04 \). For simplicity, the glass substrate could be ignored in some simulations\(^{122,123}\). The far-field scattering was calculated using the near-to-far transform (Stratton-Chu formula)\(^{124}\) on a cone oriented normal to the substrate with 48° apex angle (0.42 NA objective in scattering measurements).

When Gauss’s law was applied to the Au-silica boundaries of the nanocup, the surface charge density can be calculated by the difference between the normal components of electric field above and below the boundaries. The charge density on the Au surface was obtained by calculating the difference of the normal component of the electric field above and below the Au surface\(^{28}\).

In the SHG, the linearly polarized laser was modeled as a Gaussian profile with 90° divergence (0.7NA of the excitation objective), and the collection cone was modeled with a 128° apex angle (0.9 NA of the collection objective).
3.3.3. Setup for second-harmonic generation

Figure 3.5 Experimental setup for the measurement of SHG.

Figure 3.5 shows the detailed configuration of the sample-scanning nonlinear optical microscope we constructed for the single-nanoparticle SHG measurements. An ultrafast Ti:Sapphire laser (Mira 900, Coherent Inc.) was used to generate the fundamental beam at 800 nm (pulse duration ~ 90 fs and repetition rate ~ 76 MHz). After passing through a Faraday isolator (EOT Inc.) which allowed only one-way transmission of light, the nonzero background of laser was removed by a 4f pulse compressor working as a long pass filter. A half-wave plate (10RP52-2, Newport) and a linear polarizer (LPVIS100, Thorlabs) were used to control the polarization of the laser beam, which was then focused onto the sample using a 60× / 0.7NA microscope objective with a variable coverslip correction collar (LUCPlanFL N, Olympus). Samples were mounted on a 3 axis piezoelectric stage (P-545.3R2...
NanoXYZ, Physik Instrumente (PI) GmbH) to precisely place the desired nanocup at the focus of the excitation laser, which was attenuated by a neutral density filter (NDL-25C-4, Thorlabs) to provide a maximum power of 300 μW on focus. The second harmonic signal was collected by a 50× / 0.9NA objective (HC PL FLUOTAR, Leica); the scattering direction was analyzed by rotating a wedge cut-out mounted on the back aperture of this objective. The generated beam was filtered by a short pass filter at 785 nm (SP01-785RU-25, Semrock) to remove the fundamental wavelength, and the polarization of the SHG was analyzed by an additional polarizer (LPUV100, Thorlabs). The SHG signal was focused onto the entrance slit of a spectrograph (SpectraPro 400i, PI/Acton) by an f = 40 mm cemented achromatic doublet lens (AC254-040-A, Thorlabs), and detected by a CCD detector (PIXIS 100, PI/Acton). Two additional CCD cameras (Guppy F-146, AVT and UI-2230-C-HQ, IDS) were used to take back-scattering and transmission images to help locate the specific nanocups of interest.

3.4. Directional light scattering of light-bending nanocups

The orientation-preserved transfer procedure has enabled us to directly measure the light-scattering characteristics of the nanocup plasmon modes at the individual nanoparticle level. Previous studies of the optical properties of oriented nanocups were performed on an ensemble of nanocups embedded within PDMS in a transmission geometry, where light-refraction by the nanocup plasmon modes was measured indirectly, as a decrease in forward light scattering (180°)\textsuperscript{115}. Here we
examined optical properties of individual nanocups using the custom-built dark-field microscope (Figure 3.4).

Scattering spectra were obtained for individual nanocups (30 nm Au semishell coating on a 120 nm diameter silica core), oriented such that the axis of symmetry was either 0° or 50° from the substrate normal (Figure 3.6 and Figure 3.7). The nanocups were illuminated by p-polarized light with respect to the substrate surface and with a \( \mathbf{k} \) vector orientation described by a custom coordinate system (\( \beta \) is the inclination from the \( y \)-axis and \( \alpha \) is the rotation about the \( y \)-axis): \( \alpha \) can be varied between 0° and 50° with respect to the substrate normal while \( \beta \) remains constant at 55° throughout these experiments in order to maintain a dark-field configuration. (Note that in the same coordinate system, the nanocup will have orientations of either \( \alpha = 0° \) or -50°.)
Figure 3.6 Variable-angle darkfield scattering of individual nanocups by pure excitations. (a, b) Schematic diagrams of the experimental geometries with “pure” excitation of the fundamental plasmon modes of the nanocup (upper panels) and simulated angular scattering patterns (lower panels). The nanocup and illumination orientations are described in a custom coordinate system with angles $\alpha$ and $\beta$. (a) Pure excitation of the magnetic plasmon mode (nanocup is oriented at $[\alpha, \beta] = [0^\circ, 90^\circ]$, illumination is p-polarized and oriented with k-vector at $[\alpha, \beta] = [0^\circ, 55^\circ]$). (b) Pure excitation of the electric plasmon mode (nanocup is oriented at $[\alpha, \beta] = [-50^\circ, 90^\circ]$, illumination is p-polarized and oriented with k-vector at $[\alpha, \beta] = [40^\circ, 55^\circ]$).
Experimental (upper) and simulated (lower) scattering spectra of individual nanocups for the experimental geometries corresponding to panel a (red) and panel b (blue).

We first discuss the cases in which the \( \mathbf{E} \)-field is aligned either directly perpendicular or parallel to the nanocup axis of symmetry (Figure 3.6). The \( \mathbf{E} \)-field polarization is purely transverse when both the nanocup and the illumination \( \mathbf{k} \) vector are oriented at \( \alpha = 0^\circ \) (Figure 3.6a), while the polarization is purely axial when the nanocup is oriented at \( \alpha = -50^\circ \) and the \( \mathbf{k} \) vector is at \( \alpha = 40^\circ \) for a relative angle of 90° (Figure 3.6b). Both the experimental and simulated scattering spectra show, with good agreement, that only one plasmon mode is excited in each case (Figure 3.6c). For the case of 0° excitation (Figure 3.6a), the \( \mathbf{E} \)-field is transverse to the cup axis, and opposite charges accumulate on opposing edges of the cup opening, forming a current loop\textsuperscript{125}, or magnetic plasmon mode\textsuperscript{115} at 920 nm. By contrast in the case of 40° excitation (Figure 3.6b), the \( \mathbf{E} \)-field is oriented axially, and no current loop can be formed. Rather the electrons can only oscillate directly from the top to the rim of the cup, forming an electric dipole mode at 660 nm. Since the electric dipole mode has a higher energy than the magnetic dipole mode, a physically intuitive understanding may be obtained by noting that the electrons oscillate in a shorter distance and correspondingly a higher frequency.

To critically examine the origin of these modes, their far-field scattering patterns, representing the angular dependence of the scattering intensity (\( I \propto E^2 \)), were calculated and are shown in the lower panels of Figure 3.6a and Figure 3.6b. These scattering patterns are depicted as if viewed from the same angle as the upper
schematics so that the scattering profiles can be directly compared to the experimental geometry. The red and blue cones shown above the nanocups in the schematics represent the solid angle from which the scattered light can be collected with a 0.42 NA objective. By comparing the scattering profiles to the direction of this collection cone, one can assess the efficiency with which the scattered light radiated by a particular plasmon mode will be collected. The magnetic mode, excited in the configuration of Figure 3.6a, has the unique characteristic that it redirects, or preferentially scatters, the light along the nanocup symmetry axis regardless of the illumination incidence direction. Here, the magnetic mode scattering profile is oriented directly into the collection cone, and thus the magnetic mode is easily observed. For the case shown in Figure 3.6b, only the electric dipole mode is excited. Although the scattering profile is oriented somewhat away from the collection cone, such that the scattered light is not collected efficiently, the electric dipole mode is still observed strongly since it is the only mode excited.
Figure 3.7 Variable-angle darkfield scattering of individual nanocups by mixed excitations. (a, b) Schematic diagrams of the experimental geometries with “mixed” excitation of the fundamental plasmon modes of the nanocup (upper panels) and simulated angular scattering patterns (lower panels). The nanocup and illumination orientations are described in a custom coordinate system with angles $\alpha$ and $\beta$. (a) Configuration where the nanocup is oriented at $[\alpha, \beta] = [-50^\circ, 90^\circ]$ and the illumination is p-polarized and oriented with k-vector at $[\alpha, \beta] = [0^\circ, 55^\circ]$. (b) Configuration where the nanocup is oriented at $[\alpha, \beta] = [0^\circ, 90^\circ]$ and the illumination is p-polarized and oriented with k-vector at $[\alpha, \beta] = [50^\circ, 55^\circ]$. (c) Experimental (upper) and simulated (lower) scattering spectra of individual
nanocups for the experimental geometries corresponding to panel a (red) and panel b (blue).

When the excitation $\mathbf{E}$-field is oriented at an oblique angle where both the electric and magnetic modes can be simultaneously excited, the angular scattering profiles of each mode are far more important for interpreting the observed spectra. This scenario is shown in Figure 3.7. In Figure 3.7a, a nanocup oriented at $\alpha = -50^\circ$ is illuminated by light with incident $\mathbf{k}$ vector at $\alpha = 0^\circ$, while in Figure 3.7b, a nanocup oriented at $\alpha = 0^\circ$ is illuminated by light with incident $\mathbf{k}$ vector at $\alpha = 50^\circ$. Again, in all cases the $\mathbf{k}$ vector is kept at $\beta = 55^\circ$ in order to preserve the dark-field configuration. If one assumes substrate effects are negligible$^{122}$, then these two configurations would be identical, in terms of excitation of plasmon modes, since both the cup and illumination direction have been rotated counterclockwise about the $y$-axis by $50^\circ$. However, while the total scattering of each of these nanocups should be identical because they are excited identically, their dark-field spectra are very different (Figure 3.7c). For the $0^\circ$ excitation case (Figure 3.7a) the scattering profile of the electric dipole mode is oriented into the collection cone while the scattering by the magnetic mode is directed away from it. The $0^\circ$ excitation spectrum (Figure 3.7c) therefore shows a strong peak near 660 nm corresponding to the electric mode, while only a weak peak at 920 nm for the magnetic mode. In contrast, for the $50^\circ$ excitation case (Figure 3.7b), the scattering profile of the magnetic mode is oriented toward the collection cone, while the electric mode scatters away from it. As expected, the $50^\circ$ excitation spectrum shows
a much stronger peak for the magnetic mode than for the electric mode. It is important to note that in each of these cases, the dipole, “donut-shaped” scattering profile remains in the same plane as the illumination $k$ vector for the electric mode, but for the magnetic dipole plasmon is redirected by the nanocup orientation. The observed differences in light scattering between the electric and magnetic dipolar modes of the nanocup constitute a direct measurement of the “light-bending” properties of this structure’s magnetic dipole plasmon mode.

3.5. Second-harmonic generation from individual nanocups

3.5.1. Nanocups used for SHG

Second-harmonic generation usually requires media with reduced symmetry within the dipole limit and is thus prohibited in bulk centrosymmetric materials$^{126}$; symmetry breaking in a nanostructure can introduce new plasmon modes, leading to large local field enhancements over a broader spectral range than symmetric nanostructures$^{127,128}$. Studies of SHG in plasmonic structures and metamaterials have thus far focused on imperfect spherical structures$^{129}$, random asymmetric structures$^{130,131}$, and planar nanostructures with asymmetric geometries patterned using lithographic methods$^{132-135}$. Less studied systems, partly due to their critical fabrication challenges, are three-dimensional (3D) nanostructures, which allow for the control of SHG intensity and other properties in a highly sensitive manner.
Figure 3.8 Images and spectral response of nanocups. (a) Top-down (left) and tilted (right) SEM images of individual nanocups oriented at 50°, 30°, and 0° to the substrate normal. The overlaid yellow curves highlight the nanocup geometries. Scale bar, 100 nm. (b) Theoretical extinction spectra of these nanocups illuminated by a Gaussian beam polarized in the indicated directions. Dashed red line indicates wavelength of incident light in SHG experiments. (c) Surface charge distribution on a 0° nanocup and the magnetic field on its symmetry plane one quarter cycle later showing the magnetic dipole mode.

Nanocups, a type of 3D nanoparticle with reduced symmetry, could be a promising second-order nonlinear optical media. Au nanocups (35 nm thick Au layer on 120 nm diameter silica nanoparticles) with different orientations were controllably fabricated on glass substrates71,136 (Figure 3.8a), and then coated with a 300-nm silica layer by plasma-enhanced chemical vapor deposition (PECVD, at 300 °C for 5 minutes) to prevent damage during laser measurements. The linear
properties (Figure 3.8b) of nanocups were calculated for individual nanocups excited at normal incidence by a Gaussian source, where the electric field is parallel (p-polarization) or perpendicular (s-polarization) to the nanocup symmetry plane. Plasmonic nanocups in this size range support three plasmon modes: a magnetic dipole mode, an electric dipole mode, and an electric quadrupolar mode, in order of increasing energy. For the magnetic dipole mode at nominally 800 nm, a nanocup can be viewed as a LC resonant circuit, with the Au nanocup metal shell layer functioning as a half-coil inductor (L) and the nanocup rim forming a capacitor (C). At the frequency corresponding to the magnetic resonance, the incident electromagnetic field couples to the capacitance of the nanocup and drives a current loop in the shell layer between the opposite edges of the cup rim, generating an oscillatory magnetic field perpendicular to the electric field (Figure 3.8c and Figure 3.9). The enhanced local field at resonance contributes to the generation of the second harmonic light\textsuperscript{133,137}.

\textbf{Figure 3.9 Simulated surface charge densities on a 0° nanocup at the magnetic dipole resonance.} When excited by an 800nm laser, the charges oscillate with time, which are shown in the back (left) and side (right) views. (E\textsubscript{0} = 1 V/m). It forms an oscillating current loop (a current-driven magnetic dipole mode).
3.5.2. Second-harmonic generation measurements

SHG measurements were performed by focusing the nominally 100 fsec FWHM linearly polarized laser pulses at 800 nm wavelength onto individual nanocups mounted with the cup opening facing the incident illumination beam (Figure 3.10a). SHG experiments were performed on our sample-scanning nonlinear optical microscope (Figure 3.5), and signals were obtained from 6 individual nanocups at each orientation to ensure statistical validity. The possibility of SHG from the silica protective layer can be excluded by applying the laser spot on the clean area of the silica layer, which shows no SHG.

![Image of experimental setup and data plots](image)

**Figure 3.10 Experimental SHG by individual nanocups with different orientations.** (a) The illumination geometries of a p- (x-) or s- (y-) polarized laser irradiating individual nanocups. (b) Corresponding second harmonic conversion
efficiency versus average input power by individual nanocups for different angular orientations. Error bars, standard deviations from 6 individual particles at each orientation. (c) Polar plots (on the x-y plane) showing the angular dependence of the SHG polarization with respect to the incident polarization.

The measured SHG intensity is observed to depend on the orientation of the nanocups (Figure 3.11). The SHG conversion efficiency (Figure 3.10b), $\eta_{\text{SH}} = P(2\omega) / P(\omega)$, scales linearly as a function of the incident laser power, $P(\omega)$, with a constant slope of $\eta_{\text{SH}} / P(\omega) = P(2\omega) / P^2(\omega)$ (the power dependence of the SHG is quadratic with input laser power). The reported values take into account the transmission/reflection coefficients of the optical components and the quantum efficiency of the CCD detector. For a given excitation power, the conversion efficiency increases dramatically with nanocup angle for both p- ($\chi$-) and s- ($\gamma$-) polarized incident light. SHG from a 0º nanocup was weakly detectable, and is comparable to the SHG measured from a single centrosymmetric nanoshell (Figure 3.12). A maximum conversion efficiency of nominally $1.8 \times 10^{-9}$ was obtained for a 50º nanocup, which is higher than conversion efficiencies recently reported for other types of asymmetric nanostructures, such as asymmetric nanowire arrays or core-shell nanoparticles consisting of a nonlinear core medium and a metal shell layer\textsuperscript{66,130}. The effective susceptibility $\chi^{(2)}$ of a 50º nanocup is calculated to be 3.2 pm/V, within the range of susceptibility values of inorganic doubling crystals in widespread use, such as Potassium Dihydrogen Phosphate (KDP)(\textasciitilde 0.86 pm/V) and $\beta$-Barium Borate (BBO)(\textasciitilde 4.4 pm/V)\textsuperscript{138}; our method provides a straightforward way to fabricate SHG nanomaterials, whereas manufacturing of inorganic SHG-
active nanocrystals generally requires strict processing conditions such as well-controlled temperatures, solvent concentrations and ambient pressures\textsuperscript{139,140}.

Interestingly, the SHG intensity as a function of polarization angle reveals that the SHG signal is always p-polarized, regardless of the polarization of the fundamental beam (Figure 3.10c).
Figure 3.11 Typical SHG spectra of individual nanocups at different orientations. The p- and s-polarized lasers (at 300 μW) were incident on nanocups at 0°, 30° and 50°. The output spectra consisted of a sharply peaked SHG signal on top of a very-broad two-photoluminescence (TPPL) signal, a small fraction of the input laser leaking through the filter, and sometimes its residual edge at ~785 nm.

Figure 3.12 SHG spectrum from a single nanoshell at 300 μW laser power (silica core radius 60 nm; Au thickness 30 nm; coated with thick silica layer; resonant at ~800 nm). SHG signal is weak and just above the noise level. Inset, SEM image of a nanoshell before silica coating. Scale bar, 100 nm.

3.5.3. Theoretical modeling of second-harmonic generation

In second harmonic generation, the fundamental field \( \mathbf{E}(\mathbf{r}, \omega) \) induces the nonlinear polarization \( \mathbf{P}(\mathbf{r}, 2\omega) = \varepsilon_0 \chi^{(2)} : \mathbf{E}(\mathbf{r}, \omega) \mathbf{E}(\mathbf{r}, \omega) \), where the nonlinear susceptibility tensor \( \chi^{(2)} \) accounts for the second-order nonlinear response including both a surface term \( \chi^{(2)}_s \) and a nonlocal bulk term \( \chi^{(2)}_b \). For a structure comprised of an isotropic medium such as gold, the bulk nonlinearity will be dipole-forbidden due to symmetry \( (\chi^{(2)}_b = 0) \). For low order modes, the general behavior
of different elements in the susceptibility tensor is similar and the electric field is directed mainly in the direction normal to the metal surface\textsuperscript{142}. Therefore, SHG excited at the magnetic dipole resonance of the nanocup can be simplified to consider the one and only nonvanishing element of the tensor (surface normal component),

\[ P_{s,n}(\mathbf{r}, 2\omega) = \omega \chi_{s,nnn}^{(2)} E_n(\mathbf{r}, \omega) E_n(\mathbf{r}, \omega). \]  

Here $\chi_{s,nnn}^{(2)}$ is assumed to be a constant over the metal surface, and accordingly the harmonic field has only a surface normal component $E_n(\mathbf{r}, 2\omega) \propto P_{s,n}(\mathbf{r}, 2\omega)$. The far field $\mathbf{E}(\mathbf{r}, 2\omega)$ is then obtained by solving Maxwell’s equations and applying a near-to-far field transform (Stratton–Chu formula)\textsuperscript{124}, where the local $\mathbf{E}(\mathbf{r}, 2\omega)$ is the source. For comparison with the SHG values detected in our experiment, the intensity $I(\mathbf{r}, 2\omega) \propto E^2(\mathbf{r}, 2\omega)$ is integrated over the detection cone of the collection objective.

We considered time-harmonic fields for which the time dependence can be extracted as $\mathbf{E}(\mathbf{r}, \omega, t) = \mathbf{E}(\mathbf{r}, \omega) e^{-i\omega t}$. The calculated local field could then be described by a time-independent phasor $\mathbf{E}(\mathbf{r}, \omega) = \mathbf{E}_0(\mathbf{r}, \omega) e^{i\varphi(\mathbf{r}, \omega)}$ with spatial-variable amplitude ($\mathbf{E}_0$) and phase ($\varphi$) components.
Figure 3.13 Simulated $x$- and $y$- components of SHG fields on the outer surface of nanocups, at the instant when the cup edges have peak field magnitudes. The coordinate axes at the top indicate the 3 different view angles. The color scales assume a unity incident field and $\varepsilon_0\chi^{(2)}$. Compared to the fields on the outer surface, the fields on the inner surface are much weaker and exhibit similar field distributions. (a) 50° nanocup, (b) 30° nanocup and (c) 0° nanocup.
The origin of the observed SHG was investigated by studying the near field at the nanocup surface (Equation 3.1). The collection efficiencies of SHG from nanocups in all cases were similar, due to the high numerical aperture of the objective. Because the time-harmonic E-field is normal to the shell surface of the nanocup, its x-component \( E_x(r, 2\omega) \) exists primarily on the two sides of the nanocup along the \( x \) direction, with the \( y \)-component \( E_y(r, 2\omega) \) along the \( y \) direction (Figure 3.13). For both p- and s-polarized incident light, the \( x \)-z plane of a 50° nanocup (Figure 3.13a) is a symmetry plane for the generated second harmonic radiation. As a result, \( E_y(r, 2\omega) \) (perpendicular to \( x \)-z plane) has the same amplitude at either side of the nanocup rim, but the field is 180° out of phase at the opposite sides of the rim and therefore vanishes in the far field due to destructive interference. In contrast, the \( y \)-z plane is not a symmetry plane for this 50° nanocup SHG, thus the \( E_x(r, 2\omega) \) resulting from one side of the nanostructure is not canceled by the contribution from the field at the opposite side of the structure, and with a \( \sim 160° \) phase difference. Therefore the net contribution of SHG in the far field is purely x-polarized light. The 30° nanocup (Figure 3.13b) behaves similarly, but yields a weaker x-polarized signal since the \( E_x(r, 2\omega) \) component generated on the opposite sides of the nanocup has a smaller amplitude difference and a larger phase difference (\( \sim 170° \)), therefore a smaller net far field signal. Reduction of the nanocup angle to 0° (Figure 3.13c) results in a symmetric structure in both the \( x \)-z and \( y \)-z planes, and therefore a vanishingly small macroscopic second harmonic signal in the far field, in agreement with our experimental results.
Additionally, we found that SHG efficiency was higher for p-polarized than for s-polarized excitation for all nanocup orientations (Figure 3.10b). The harmonic intensity depends on the spatial distribution of the fundamental field $|E_n(r, \omega)|$ (Equation 3.1), with hot spots mainly along the $x$ direction for p-polarized excitation and along the $y$ direction for the s-polarized laser (Figure 3.14). Since the nonlinear responses along the $y$ direction will cancel due to symmetry, SHG resulting from field enhancements along the $x$ direction will dominate. These $x$-direction field enhancements will be largest for p-polarized excitation, and therefore p-polarized excitation will produce a stronger SHG signal than s-polarized excitation. By applying the near-to-far field transform, we quantified the SHG efficiency for p-polarized excitation as 1.76 times that for s-polarized excitation, which is close to the experimental result of 1.58 (Figure 3.10b).

It is interesting to note that, based on the calculation, there is an optimal nanocup angle, $\sim 70^\circ$, for SHG efficiency: while the SHG efficiency increases with increasing angle, the coupling of light to the nanostructure is reduced at larger angles due to the reduced coupling of light (reduced cross section) to the structure.
However, this theoretically optimal SHG angle is not easy currently with our fabrication methods. Modifying our fabrication method or developing large-area materials with this SHG motif to allow for tilting the sample, would make this slightly steeper angular range readily accessible.

### 3.5.4. Directional emission of second-harmonic light

The SHG from a nanocup is emitted with a profile controlled by nanocup orientation, regardless of the excitation direction or polarization. This directional scattering results from the resonant enhancement of the SHG by the magnetic dipole mode, which scatters the SHG in donut-shaped profiles with the “optimized” emission close to the nanocup orientation (Figure 3.15a). Since the local SHG E field, originating from the “SHG dipole” formed by the two hot spots on the x-sides of the nanocup, is perpendicular to the cup axis in the x-z plane, the SHG wave vector, transverse to the E field, forms a donut shape along the direction of the cup axis (perpendicular to the dipole). This directional scattering was observed experimentally by mounting a rotatable wedge-shaped aperture (a thin, round piece of metal with a 20° wedge-shaped cutout) at the back aperture of the collection objective (Fourier plane) perpendicular to the optical axis. The SHG intensity as a function of wedge-opening angle is shown in the polar plots of Figure 3.15b; nearly all the SHG photons are emitted in a single direction, consistent with our theoretical analysis of the SHG angular dependence. The effect of a large numerical aperture of the objective on the angular SHG emission was found to create only a nominal difference from our electrodynamic simulation results obtained when illuminating
the nanocup with an incident plane wave. The protective silica coating of the nanocups has a half-sphere outer-profile following the geometry of a nanocup, thus the light redirection on the silica-air interface due to refraction can be ignored.

Figure 3.15 SHG scattering patterns by a 50° nanocup, for p-polarized (upper) and s-polarized (lower) incident light. (a) Calculated far-field angular dependence of the scattered SHG intensity (I ∝ E^2) relative to the incident laser (red arrows). These SHG signals are emitted with a peak in a specific direction (blue arrows) close to the cup-axis direction (yellow arrows). (b) Experimental result showing a directional radiation of SHG signals consistent with the theoretical prediction. The red coordinate axes indicate the polarization of the normally incident laser.

3.6. Conclusions

A simple, robust, and generalizable method for transferring nanocups from their growth substrate to receiver substrates, which precisely preserves the 3D
orientation of the nanoparticles, has been demonstrated. This technique could be adopted to transfer a wide variety of both geometrically and chemically asymmetric nanostructures onto any substrate where a thin layer of oxide is either present or can be grown for a specific material or device of interest.

Optical spectra of the magnetic and electric dipole plasmon modes of individual, oriented nanocups were obtained using variable-angle dark field microscopy. A pure dipole mode is excited when the electric field component of incident light is either transverse or parallel to the cup axis. When this field is at an oblique angle, however, a mixture of both dipole modes can be excited, resulting in collection angle-dependent scattering spectra. Variable-angle dark field scattering measurements have enabled us to directly observe the unique light-bending properties of this asymmetric 3D “Janus” nanoparticle. We anticipate that the optical properties observed in these nancups will provide new methods for guiding and manipulating light, and may give rise to new types of optical components and applications.

It is possible to fabricate plasmonic motifs that function as efficient sources of second harmonic light. Rather than relying on crystalline SHG materials grown by traditional methods, our results open up the possibility for creating synthetic SHG media that can be produced using novel yet straightforward nanofabrication techniques. This same approach can also be used to design media for other, related second-order nonlinear optical processes such as sum- or difference-frequency mixing, optical rectification, or the electro-optic effect. Numerous photonic devices
based on these processes, such as optical parametric oscillators or amplifiers, electro-optic or acousto-optic modulators, could be produced for specific applications at correspondingly lower cost. By utilizing the inherent geometric tunability of their plasmon resonances, materials based on this motif can be designed for the frequency mixing of light at unique wavelengths, or wavelength combinations, of interest. Either as individual nanostructures which could serve as subwavelength light sources or as multilayer arrays serving as macroscopic frequency-mixing media, this approach promises a range of uses not yet achievable with current second-order nonlinear optical materials. Based on the our results, it is clear that the robust chemical stability and UV transmission of these structures makes this approach highly promising for the generation of short wavelength UV light using visible or near-IR sources. Artificial frequency-mixing media could just as straightforwardly be designed for the infrared, to be easily integrated into silicon photonics, for on-chip optical measurements requiring the cross-correlation of ultrafast optical signals, for example. Considering that the resonant wavelength of nanocups can be tuned according to their dimensions, these findings will enable the design of new, practical second-order nonlinear optical materials for wavelengths where few, if any, nonlinear optical materials have been identified.
Plasmonic nanoclusters, an ordered assembly of coupled metallic nanoparticles, support unique spectral features known as Fano resonances (FR) due to the coupling between their subradiant and superradiant plasmon modes. Within the Fano resonance, absorption is significantly enhanced, giving rise to highly localized, intense near fields with the potential to enhance nonlinear optical processes. We designed a structure supporting the coherent oscillation of two distinct FRs within an individual plasmonic nanocluster. We show how this coherence enhances the optical Four-Wave Mixing (FWM) process in comparison to other double-resonant plasmonic clusters that lack this property. A model that explains the observed FWM features is proposed, which is generally applicable to any third-order process in plasmonic nanostructures. With a larger effective
susceptibility $\chi^{(3)}$ relative to existing nonlinear optical materials, this coherent double-resonant nanocluster offers a new strategy for designing high-performance third-order nonlinear optical devices, such as optical processors that transform two incoming light signals into output of a third color.

4.1. Introduction

Traditionally, nonlinear optical phenomena have relied on crystalline media that combine material susceptibilities and phase matching to optimize nonlinear optical processes. It has been shown that certain plasmonic nanostructures can produce an enhanced nonlinear response when excited at their resonant frequency$^{17,144}$. Phase-matching requirements$^{145-147}$ for nonlinear optics in macroscopic media are usually optimally fulfilled at nanoscale dimensions ($\text{sinc}^2 (\Delta k z / 2) \sim 1$ for small $z$, where $z$ is the propagation distance through the medium), and the details will be discussed in section 4.2.4. For plasmonic nanostructures, the most important property for the enhancement of nonlinear properties is their increased local fields at resonance, which can provide larger effective susceptibilities than their intrinsic material susceptibility.

In the third-order nonlinear process of four-wave mixing (FWM), two external fields $E_0(\omega_1)$ and $E_0(\omega_2)$ are simultaneously incident on the nanostructure, inducing local fields $E(\omega_1)$ and $E(\omega_2)$; absorbing two $\omega_2$ and one $\omega_1$ photons and emitting a photon at $\omega_{\text{FWM}} = 2\omega_2 - \omega_1$ (Figure 4.1)$^{145}$. The electromagnetic FWM enhancement $G_{\text{FWM}} = |E(\omega_2)/E_0(\omega_2)|^4 \cdot |E(\omega_1)/E_0(\omega_1)|^2$ thus depends on the field enhancements at
the input frequencies. Fano-resonant structures can exhibit very large local field enhancements\textsuperscript{148,149}, making these structures prime candidates for nonlinear frequency generation. While previous studies of nonlinear plasmonics employed nanostructures with a single dipolar resonance\textsuperscript{150,151}, in a multi-input process such as FWM, the conversion efficiency is expected to be further enhanced if the plasmon modes of the nanostructure are resonant with both input frequencies\textsuperscript{152}.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fwm_config.png}
\caption{FWM configuration in a single nanocluster, where two coherent inputs at frequencies $\omega_1$ and $\omega_2$ generate a plasmon-enhanced FWM signal $\omega_{\text{FWM}} = 2\omega_2 - \omega_1$.}
\end{figure}

In this chapter, we demonstrate highly efficient FWM from a plasmonic nanocluster that supports two distinct FRs\textsuperscript{96,148,149,153-155}. When excited by a coherent source, the two spatially coherent FRs oscillate collectively, in a mixed frequency analog to a two-state quantum system, where the electric fields from the two modes add coherently, resulting in strong field enhancements. In comparison, plasmonic nanostructures with resonances at the same two frequencies that lack
coherence are found to give rise to lower FWM efficiencies, while providing similar linear optical properties.

4.2. Methods and instruments

4.2.1. Sample preparation and characterization

The structures were fabricated by standard positive-resist electron beam lithography for patterning a 50 nm thick Au on a 1 nm Ti adhesive layer, which had first been evaporated onto an ultra-smooth fused silica substrate (surface finish 10/5, SVM). The fabricated nanoclusters were arranged in a 5 × 5 array with 10 μm intercluster distances to avoid coupling effects during single particle measurements. Dark field scattering spectra were collected by a custom-built microscope with ~35° incidence (Microscope: Axiovert 200 MAT, Zeiss; Objective: 50×/0.55NA Epiplan-Neofluar, Zeiss; Spectrograph: SP2150, PI/Acton; CCD: PIXIS 400BR, PI/Acton).

4.2.2. Numerical simulation

Numerical studies of the electromagnetic responses were performed using the finite-difference-time-domain (FDTD) commercial software (Lumerical FDTD Solutions 7.5.3) with normal incidence. The top-view geometries were chosen to closely match SEM images, and the heights used were the Au thickness deposited during sample fabrication. The empirical bulk dielectric function\(^{31}\) was used for Au and \(\varepsilon = 2.10\) for the infinite fused silica substrate. Charge density was obtained by
calculating the difference of the normal component of the electric field above and below the Au surface (Gauss’s law).

### 4.2.3. Experimental setup

Figure 4.2 shows the configuration of the sample-scanning nonlinear optical microscope we constructed for the single particle FWM measurements. A mode locked laser system (Coherent Inc.) consisting of a Ti:Sapphire oscillator (Mira 900), a regenerative amplifier (RegA 9000) and an OPA (Model 9400) was used. A small portion of RegA output was passed through a 800 nm bandpass filter (FF01-800/12-25, Semrock) and the OPA Signal was passed through two 670 nm bandpass filters (FB670-10, Thorlabs), serving as the two excitation beams (both pulse duration ~ 200 fs; repetition rate ~ 247 MHz). Each polarization was controlled by a half-wave plate (10RP52-2, Newport) and a linear polarizer (LPVIS100, Thorlabs), and their intensity was attenuated by two neutral density filters (NDL-25C-4, Thorlabs). These two beams were then superimposed spatially using a dichroic mirror (DMLP605, Thorlabs). A computer-controlled delay stage (ILS200CHA, Newport) was inserted into the 800 nm path to overlap the pulses in time. The linearly (x-) polarized, collinear and coherent beams were then focused onto the sample with a spot size of ~ 1 μm using a 50× / 0.8NA objective (HC PL FLUOTAR, Leica). Samples were mounted on a three-axis piezoelectric stage (P-545.3R2 NanoXYZ, Physik Instrumente (PI) GmbH) to position the desired nanocluster precisely at the beam focus. The FWM light generated by the structure was collected by a 60× / 0.7NA microscope objective with a variable coverslip correction collar
(LUCPlanFL N, Olympus), then transmitted through a 633 nm shortpass filter (SP01-633RU-25, Semrock) to remove any residual light at the excitation wavelengths. The FWM polarization was analyzed by an additional polarizer (LPUV100, Thorlabs). It was focused onto the entrance slit of a spectrograph (SpectraPro 400i, PI/Acton) by an $f = 40$ mm cemented achromatic doublet lens (AC254-040-A, Thorlabs), and detected by a CCD detector (PIXIS 100, PI/Acton). Two additional CCD cameras (Guppy F-146, AVT and UI-2230-C-HQ, IDS) were used to obtain images of the back-scattered and transmitted light to assist in locating the specific nanocluster of interest on the sample.

Figure 4.2 Experimental setup for the FWM measurement. BPF: bandpass filter; $\lambda/2$: half-wave plate; SPF: shortpass filter.
4.2.4. Phase-matching conditions

On our setup, both incident beams can be regarded as ideal Gaussian beams (diameter $d \sim 3.5$ mm), which were transmitted through the back-aperture of the excitation objective (diameter $D \sim 6$ mm) with filling factor $f_0 = d / D = 0.583$. The objective focuses both beams into secondary Gaussian beams, in approximation. We optimized the signal intensity by placing the nanoparticle at the laser focus with a XYZ piezoelectric stage (Figure 4.3a). For the 800 nm beam, its waist radius $w_0 \approx \lambda / (f_0 \text{NA} \pi) = 546$ nm and the Rayleigh range $z_R = \pi w_0^2 / \lambda = 1.170 \mu m$.

Figure 4.3 (a) Scheme of a nanoparticle in the center of a tightly focused Gaussian beam by the excitation objective. (b) The wavevector diagrams for the degenerate four-wave mixing.

First we examine the edge point (p) of the nanostructure we are going to measure, where $z = 25$ nm is the axial distance from the beam waist plane and $r \approx 300$ nm is the radial distance from the $z$-axis. The wavefront radius at p is $R(p) = z [1 + (z_R / z)^2] = 54.85$ µm, and the angle between the wave vector $k_1$ and the $z$-axis is $\gamma_1 = \sin^{-1} [r / R(p)] = 0.31^\circ$. Likewise, we calculate $\gamma_2 = 0.45^\circ$ for the 670 nm beam.
Any other positions on the nanocluster should have even smaller laser incident angles. Also, the localized plasmon fields should be perpendicular to the metal surfaces. Thus both beams behave very similarly to normal-incident plane waves on this nanocluster. (In case of non-zero incident angles, one can follow the method in the reference\textsuperscript{15} to calculate the FWM emission angles.)

The momentum of the incoming and outgoing photons has a mismatch of $\Delta k = 2k_2 - k_1 - k_{\text{FWM}} = -1.987 \times 10^{-3}$ rad nm\(^{-1}\) on the z-direction (Figure 4.3b; the plotted outgoing photon direction is the most probable direction as it minimizes the momentum mismatch). We believe the additional momentum could be provided by the lattice of the nanoparticle. We then calculated the phase-matching factor (efficiency) to be $\text{sinc}^2 \left( \frac{\Delta k \cdot z}{2} \right) = 0.9919 \approx 1$, which means a good phase-matching can be achieved for nanoparticles with an extremely small dimension $z$.

If the nanostructure edge was 200 nm away from the beam waist due to larger particle size or laser defocusing, the largest incoming angles (at this edge point) are $\gamma_1 = 2.44^\circ$ and $\gamma_2 = 3.44^\circ$. The outgoing FWM is calculated\textsuperscript{15} to be propagating at $\theta = 1.76^\circ$, and the corresponding phase-matching factor is $0.9917$ for this edge point. This result indicates the phase-matching in FWM is not sensitive to the nanostructure position in the laser focus.

If the incident laser beams fill the back-aperture of the excitation objective, they will be tightly focused into secondary Gaussian beams in the diffraction limit. In this case the incident angles on the edge point are $\gamma_1 = 2.70^\circ$ and $\gamma_2 = 3.85^\circ$, and the output angle is $\theta = 1.98^\circ$. The phase-matching factor is calculated to be $0.9917$. 
4.2.5. Pulsed laser annealing

All nanostructures underwent a pulsed laser annealing procedure using 3.8 µW total power for 4 minutes to stabilize the nanostructure prior to FWM data collection (Figure 4.5).

![Figure 4.4 Pulsed laser annealing by two beams of total 3.8 µW.](image)

(a) FWM signal during this process was observed to increase slightly and smoothly in approximately the first 150 seconds, gradually approaching stable. (b) Normalized dark-field spectra of the nanostructure before (red) and after (blue) irradiation. No significant changes were observed upon irradiation. The spectral features became more pronounced due to the improvement of Au crystal structure and subsequent stronger plasmon resonances corresponding to the annealing effects.

4.3. Coherent Fano resonant nanocluster

We designed a nanocluster, which has two FRs tuned to the two excitation frequencies needed for FWM. The nanocluster, composed of a central disk, an inner ring of disks and a degenerate outer ring of disks (Figure 4.5a, inset), belongs to the D_{6h} symmetry group. Its measured and calculated linear scattering spectra (Figure 4.5a) reveal two prominent scattering minima. The origin of these spectral
dips can be understood by examining the charge densities $\rho(r, t)$ at the spectral minima (Figure 4.5b), where the structure supports oscillations of the central disk and the inner and outer rings of disks. At the minimum at 800 nm wavelength, the center particle dipole oscillates out-of-phase with both the inner and outer collective ring oscillations. However, at the minimum at 670 nm wavelength, the center particle dipole oscillates out-of-phase with the inner ring but in-phase with the outer ring.

**Figure 4.5 Properties of double Fano resonant plasmonic nanocluster.** (a) Experimental (black) and calculated (green) dark-field scattering spectra of the nanocluster obtained with horizontal (x-) polarization. Two prominent minima at 800 and 670 nm are labeled by brown and orange dashed lines. The inset shows an SEM image of the nanocluster. Scale bar, 100 nm. All disk diameters are 120 nm with 50 nm heights and ~18 nm gaps. Superimposed yellow dashed lines denote the central disk, inner and outer disk rings of the nanocluster. Red arrow indicates the incident polarization. (b,c) Snapshots of simulated charge densities $\rho(r, t)$ on the top
surface of the nanocluster for the 800 and 670 nm FRs at $t = 0$ (b), and for the coherent state at 3 different times (c). Black arrows correspond to local E-field directions.

When both FRs of the nanocluster are excited simultaneously (by two coherent beams at 800 nm and 670 nm), the plasmons oscillate in a mixed frequency “coherent mode”. In this mode, the charge oscillation of the central disk is out-of-phase with the inner ring, but switches rapidly between in-phase and out-of-phase with respect to the outer ring, in each case corresponding to the oscillatory behavior of one of the FRs (Figure 4.5c). By performing a discrete Fourier transform\textsuperscript{158} on the time series of charge densities $\rho(r, t)$ at each position $r$, this coherent state, with a period $T_{\text{coherent}} \sim 13.35$ fs, can be decomposed into two discrete FR eigenmodes with $\rho(r, \omega)$ at 800 ($T_1 \sim 2.67$ fs) and 670 nm ($T_2 \sim 2.23$ fs). The coherent mode has a period equal to the time when the two discrete FRs have the same phase ($T_{\text{coherent}} \approx 5T_1 \approx 6T_2$), undergoing $\sim 15$ periods during the pulse duration used in the experiment ($\tau \sim 200$ fs). For the coherent state, enhanced local fields at multiple resonant frequencies overlap not only in time but also in space, contributing to the nonlinear optical wave-mixing. Figure 4.6 shows 36 equally spaced frames (one period) of charge distributions for the coherent mode, with features on the central disk, inner and outer rings a mixed result of two FRs.
Figure 4.6 Periodic evolution of charge distributions for one period of the double FR coherent mode.

4.4. FWM experiment and theory

FWM measurements were performed on individual nanoclusters (in the x-y plane) with linearly (x-) polarized incidences. Only the case where both lasers were x-polarized was investigated, since this configuration generated the strongest FWM
signal. The total average applied power ranged from $1 - 3 \, \mu W$ (peak intensities of $0.13 - 0.4 \, GW \, cm^{-2}$), and measurements were performed on 6 different nanoclusters to ensure statistical validity.

![Graph of FWM signal and spectra](image)

**Figure 4.7 Typical FWM signals generated by $P_1 = 1 \, \mu W$ and $P_2 = 1.9 \, \mu W$.** (a) Spectra of the two input laser beams (red), and a FWM output signal at $\lambda_{FWM1} = 2 \lambda_2 - \lambda_1 = 576 \, nm$. The small spectral feature at ~ 615 nm is the edge of the short pass filter used to block the excitation beams. (b) Another FWM signal generated at $\lambda_{FWM2} = 2 \lambda_1 - \lambda_2 = 993 \, nm$. A 900nm longpass filter (FEL0900, Thorlabs) was used to remove the excitation wavelengths.

A characteristic FWM output spectrum consists of a sharply peaked signal centered at $\lambda_{FWM} = 576 \, nm$ with $\Delta \lambda_{FWM} = 5.3 \, nm$, on top of a significantly weaker, broadband multiphoton luminescence (MPL) signal\textsuperscript{159} (Figure 4.7a, green). The Gaussian lineshape FWHM of the incident beams was measured to be $\Delta \lambda_1 = 5.3 \, nm$ and $\Delta \lambda_2 = 5.5 \, nm$ (Figure 4.7a, red). If one considers the timescale of FWM generation as being ~ $\tau$, the estimated FWM bandwidth should be proportional to $1/\tau$, which is close to the observed result. Additionally, we observed another FWM
signal centered at $\lambda_{\text{FWM2}} = 993$ nm with $\Delta \lambda_{\text{FWM2}} \approx 4$ nm (Figure 4.7b), due to the complementary $\omega_{\text{FWM2}} = 2\omega_1 - \omega_2$ process. Since this signal lies at the limit of our CCD detection range (CCD quantum efficiency drops dramatically beyond 950 nm), we focused on the 576 nm FWM signal only.

The FWM signal was observed to follow a cubic power law behavior as a function of total input power ($P_{\text{tot}} = 1.05 \sim 2.9 \mu W$, using $P_1 : P_2 = 1 : 2$) (Figure 4.8a). This response scales quadratically with the $P_2$ input power ($P_2 = 0.84 \sim 1.9 \mu W$, using $P_1 = 1.1 \mu W$), and linearly with $P_1$ input power ($P_1 = 0.4 \sim 1 \mu W$, using $P_2 = 1.9 \mu W$). All data points in this regime follow a simple power law, indicating that we are not in a regime of plasmon saturation\textsuperscript{16}. Increasing the input power further causes

Figure 4.8 Power dependences and polarization of FWM signals. (a) Normalized FWM power versus normalized total input power $P_{\text{tot}}$ (black squares), $P_2$ only (red circles) and $P_1$ only (blue triangles) on a log-log scale. Dashed lines are linear fits of the experimental data. Error bars represent the standard deviations of signals from six individual nanoclusters, arising mainly from fabrication irregularities. (b) Polar plots show the measured (black circles) and calculated (green curve) FWM polarization by two x-polarized lasers. The latter is calculated based on Figure 4.9c.
optical damage of the sample: when this occurs, the FWM signal gradually and irreversibly decreases. We calculated the nonlinear cross section for the nanocluster to be $\sigma^{(3)} = 1.41 \times 10^{-12}$ cm$^2$, and its effective susceptibility $\chi^{(3)}$ is $4.65 \times 10^{-15}$ m$^2$ V$^{-2}$ (3.35 $\times 10^{-7}$ esu), taking into account the instrument efficiency$^{145}$. This value is much larger than that of nonresonant dielectrics$^{145}$ ($10^{-22} \sim 10^{-18}$ m$^2$ V$^{-2}$), semiconductors$^{160}$ ($\sim 10^{-12}$ esu) or nonlinear crystals$^{161}$ ($10^{-14} \sim 10^{-13}$ esu), and among the highest reported for metallic nanoparticles$^{162-165}$ ($10^{-12} \sim 10^{-7}$ esu), which we attribute to the enhancement provided by the coherently coupled FRs in the nanostructure.

The polarization dependence of the FWM signal has an unusual butterfly-like profile, with its maximum intensities near 20$^\circ$ and 160$^\circ$ (Figure 4.8b, black circles). The FWM light has a nonzero $y$-component, despite the fact that both pump lasers are purely $x$-polarized. These results are distinct from previous studies$^{15,151}$ where the FWM was linearly polarized for either parallel or oblique incidence.

We have developed a simple model to explain the origin and characteristics of FWM on a plasmonic nanocluster. In degenerate FWM, the two local fields $\mathbf{E}(r, \omega_1, t)$ and $\mathbf{E}(r, \omega_2, t)$ induce a nonlinear polarization

$$P^{(3)}(r, \omega_{\text{FWM}}) = \varepsilon_0 \chi^{(3)} \left(-\omega_{\text{FWM}}, \omega_2, \omega_2, -\omega_1 \right) \cdot \mathbf{E}(r, \omega_2) \mathbf{E}(r, \omega_2) \mathbf{E}^*(r, \omega_1),$$

where $\mathbf{E}(r, \omega) = \mathbf{E}(r, \omega, t)/e^{-i\omega t}$ is the amplitude of the time-harmonic fields; the susceptibility tensor $\chi^{(3)}$ accounts for the intrinsic third-order nonlinear response of the material(s), and in turn gives rise to a FWM field $\mathbf{E}(r, \omega_{\text{FWM}}) = P^{(3)}(r, \omega_{\text{FWM}}) /$
\(\omega n^2(\omega_{\text{FWM}})\) radiating at \(\omega_{\text{FWM}} = 2\omega_2 - \omega_1\). When both incoming frequencies are incident on the nanocluster and resonant with its FRs, their enhanced local fields overlap spatially in the nanocluster gap regions (Figure 4.9a). These intense fields give rise to the large effective \(\chi^{(3)}_{16,150}\). At optical frequencies, plasmon-enhanced local fields are confined within a thin layer on each metal surface, in the direction of the surface normal with a dominant surface nonlinearity, thus equation 4.1 can be transformed into the surface coordinate system where only the normal component is considered:

\[
E_{s,n}(\omega_{\text{FWM}}) = \chi^{(3)}_{s,n,m,n,m} E_{s,n}^2(\omega_2) E_{s,n}(\omega_1) / n^2(\omega_{\text{FWM}})
\]

where \(\chi^{(3)}_{s,n,m,n,m}\) is assumed to be a constant over the metal surfaces for simplicity.

Because the generated FWM field oscillates rapidly with time, the measured signal is the time-integrated intensity \(I(\omega_{\text{FWM}}) \propto E^2(\omega_{\text{FWM}})\). A generalized formula is obtained for FWM fields enhanced by plasmonic nanostructures (Figure 4.9b):

\[
\langle \tilde{E}_{s,n}(\omega_{\text{FWM}}, t) \rangle = \left[ \frac{1}{T} \int_0^T E_{s,n}(\omega_{\text{FWM}}) \cos^2(\omega_{\text{FWM}} t) dt \right]^{1/2} = \sqrt{2} \chi^{(3)}_{s,n,m,n,m} E_{s,n}^2(\omega_2) E_{s,n}(\omega_1) / n^2(\omega_{\text{FWM}}).
\]
Figure 4.9 FDTD calculated near-field maps of the nanocluster. (a) The field enhancement intensity ($E^2$) evaluated at mid-height of the nanocluster at $\lambda_1 = 800$ nm (left) and $\lambda_2 = 670$ nm (right). (b) Time-averaged FWM fields generated on the Au nanocluster surfaces. The color scales assume unity incident fields and $\chi^{(3)}/n^2$. In (a) and (b), the overlaid disk indices are guides to the eye; i, ii and iii points to three hotspots. (c) Time-averaged $x$- (left) and $y$- (right) components of the FWM fields on the nanocluster surfaces.

The polarization of each FWM photon is perpendicular to the Au side walls in the $x$-$y$ plane, provided that the photon polarization is the same as its local fields. The FWM field map can be decomposed into $x$- and $y$- components (Figure 4.9c), and then the far field FWM polarization is obtained by integrating over the Au surfaces,

$$I_{FWM}(\theta) \propto \int \left[ |\langle \vec{E}_x(\omega_{FWM}, t) \rangle| \cos \theta | + |\langle \vec{E}_y(\omega_{FWM}, t) \rangle| \sin \theta \right]^2 ds$$

where $\theta$ is the angle between the output polarizer and the $x$-axis. The calculated FWM polarization polar plot (Figure 4.8b, green curve) has a small $y$-component at
\(\theta = 90^\circ\) and a much larger \(x\)-component that is slightly reduced at \(\theta = 0^\circ\). The degree of polarization, \(P_d = \frac{|I_x - I_y|}{|I_x + I_y|} = 0.64\), is consistent with experimental measurements. This unusual polarization behavior results because some FWM hotspots are not parallel to either the \(x\)- or \(y\)-axis (e.g. i, ii and iii in Fig. 3B) and therefore contribute partially to each of the orthogonal components of the emitted light.

4.5. FWM control experiments on two other nanoclusters

To further investigate the specific effect of coherent FRs on the enhancement of optical FWM, two nanocluster “controls” were designed. (I) one with two coherent bright modes, where charges oscillate in dipole-dipole (antibonding) and dipole-quadrupole modes (Figure 4.10a and Figure 4.10c), and (II) one with two spatially incoherent (decoupled) oscillations of a subradiant heptamer dark mode and a dipole bright mode supported by the corner disks (Figure 4.10b and Figure 4.10d). In all cases, the plasmon resonant features were designed to correspond to the two FWM input frequencies. Besides the double-resonant conditions fulfilled by these structures, there are other factors affecting the FWM efficiency, which we attempt to maintain as consistently as possible for all three cluster geometries. Since larger particles usually give rise to stronger signals, all structures were designed with same volume of Au for comparison. The sizes of the gaps also strongly affect the nonlinear responses of the clusters, where stronger signals come from smaller
gaps\textsuperscript{150,152,167}, thus they were made identical in all three geometries, except for the ~80 nm decoupling spacing in case II (Figure 4.10a and Figure 4.10b, insets).

![Figure 4.10 FWM control experiments.](image)

(a, b) Experimental (black) and calculated (green) dark-field scattering spectra of two nanoclusters for control experiments, obtained with horizontal (x-) polarization. Both structures have double resonances, indicated by the brown (800 nm) and orange (670 nm) dashed lines. Insets are SEM images of these nanoclusters. Scale bars, 100 nm. Red arrows indicate the incident polarization. In (a), all disk diameters are 144 nm with ~18 nm gaps. In (b), the nanocluster is formed by a heptamer surrounded by four corner disks. Heptamer disks are 135 nm in diameters with ~18 nm gap; corner disks are 124 nm with ~80 nm spacing from heptamer disks along x direction. (c, d) Simulated charge distributions (left) and field enhancement intensities $E^2$ (right) for two control cases at $\lambda_1 = 800$ nm (brown dashed box) and $\lambda_2 = 670$ nm (orange dashed box). Black arrows indicate local E-field directions. The overlaid disk indexes are guides to the eye.
Figure 4.11a shows the time-averaged FWM fields of these two control nanoclusters. By integrating the square modulus of the FWM field over the disk surfaces shown in Figure 4.9b or Figure 4.11a, relative FWM cross sections ($\propto$ conversion efficiencies) can be calculated for these three structures, which agree well with the measured FWM intensities by $P_1 = 1$ $\mu W$ and $P_2 = 1.9$ $\mu W$ (Figure 4.11b). Comparison between all three cluster geometries shows that while all cluster geometries show a significant FWM enhancement, the structure supporting two coherent FRs provides the highest FWM enhancement among these three types of double-resonant structures by nominally a factor of 2 to 4. We attribute this as being due to the reduced light scattering and intense local fields of the coherently coupled (spatially overlapping) FRs relative to the other cluster geometries. Control (II), where the two resonances are spatially decoupled, has the lowest FWM enhancement.

Figure 4.11 Comparison of FWM on different nanoclusters. (a) Time-averaged FWM fields on control nanocluster surfaces. The color scales assume unity incident fields and $\chi_3^{(3)}/n^2$. The overlaid disk indexes are guides to the eye. (b) Measured
FWM intensities (error bars) and calculated FWM cross-sections (green bars) for all three structures.

4.6. Conclusions

In conclusion, we have designed a plasmonic nanocluster that supports two FRs in a coherent state, a temporally oscillating superposition of two spatially coherent subradiant modes. Time-resolved field investigations reveal the ultrafast dynamics of this coherent state, suggesting that dynamical studies may lead to a greater understanding of coherence in plasmonic nanocomplexes. We have also shown that this nanostructure provides an outstanding resonant enhancement of optical four-wave mixing, providing significantly greater enhancement of this process than similarly sized nanoclusters with double resonances of different types.

The extremely large effective $\chi^{(3)}$ for this nanocluster strongly suggests its use in high-performance synthetic nonlinear optical materials, which would provide new strategies for sensors and detectors, new types of optoelectronic devices, and building blocks for optical information processing. Information processing that takes place inside today’s computers, smartphones and tablets is electronic. Each of the billions of transistors in a computer chip uses electrical inputs to act upon and modify the electrical signals passing through it. Optical information processing, using light instead of electricity, could allow for computers that are both faster and more energy-efficient.
Surface-enhanced Coherent Anti-Stokes Raman Scattering using a Plasmonic Fano Resonance

Plasmonic nanostructures are of particular interest as substrates for the spectroscopic detection and identification of individual molecules. Single-molecule sensitivity Raman detection has been achieved by combining resonant molecular excitation with large electromagnetic field enhancements experienced by a molecule associated with an inter-particle junction. Detection of molecules with extremely small Raman cross-sections ($\sim 10^{-30} \text{ cm}^2 \text{ sr}^{-1}$), however, has remained elusive. We show that coherent anti-Stokes Raman spectroscopy (CARS), a nonlinear spectroscopy of great utility and potential for molecular sensing, can be used to obtain single-molecule detection sensitivity, by exploiting the unique light harvesting properties of plasmonic Fano resonances. The CARS signal is enhanced by $\sim 11$ orders of magnitude relative to spontaneous Raman scattering, enabling the
detection of single molecules, which is verified using a statistically rigorous bi-analyte method. This approach combines unprecedented single-molecule spectral sensitivity with plasmonic substrates that can be fabricated using top-down lithographic strategies.

5.1. Introduction

Raman spectroscopy measures the vibrational modes of a molecule, providing information about its molecular structure, conformation, and temperature. Surface enhanced Raman Scattering (SERS)\textsuperscript{89,168,169} has advanced to the detection limit of individual resonant molecules when the molecule is closely associated with the nanoscale junction between chemically fabricated nanoparticles\textsuperscript{25,170-177}. Here two enhancement mechanisms are at play: the enhanced Raman cross-section of a molecule when the excitation laser is resonant with an electronic excitation of the molecule; and the extremely large local electromagnetic field enhancement generated by optically exciting the collective plasmon mode of the two closely adjacent nanoparticles. Due to the magnitude of the electromagnetic enhancement achievable in nanoparticle junctions, it appears doubtful whether this same approach could be used to generally detect random “unknown” molecules at the single-molecule level.

One could, however, improve molecular detection sensitivity further by combining plasmonic (SERS) enhancements with coherence. Coherent anti-Stokes Raman scattering (CARS)\textsuperscript{178-182} is a third-order nonlinear optical process (a specific
type of four-wave mixing spectroscopy) that employs molecular coherence. In CARS, the pump ($\omega_P$) and Stokes ($\omega_S$) fields interact coherently through the third-order polarizability of the dipole-forbidden vibronic modes of a molecule, generating an anti-Stokes signal $\omega_{\text{AS}} = 2\omega_P - \omega_S$ with the intensity dependence of a third-order nonlinear optical process:

$$I_{\text{CARS}} \propto |\chi^{(3)}|^2 I_P^2 I_S.$$  \hspace{1cm} (5.1)

When the frequency difference $\omega_P - \omega_S$ coincides with a Raman (dipole-forbidden vibrational) band of the molecule, the CARS signal is resonantly enhanced as a scattering peak. This two-beam, coherent process is usually orders of magnitude stronger than spontaneous Raman Scattering\textsuperscript{183}. Coherent and spontaneous Raman Scattering processes are diagrammed in Figure 5.1a.
Figure 5.1 Different types of Raman processes and the SECARS configuration. (a) Energy level diagram shows four types of Raman processes of a molecule. The arrow thickness indicates the transition strength. (b) SECARS configuration of two diluted molecules on a nanoquadrumer. A single-wavelength pump laser ($\omega_P$) and a supercontinuum Stokes laser ($\omega_S$) generate an enhanced anti-Stokes scattering ($\omega_{AS}$) of a molecule in the quadrumer central gap.

The sensitivity of CARS can be increased even further by designing an appropriately resonant plasmonic substrate\(^{184}\). If the input ($\omega_P, \omega_S$) or output ($\omega_{AS}$) frequencies in CARS are in resonance with the collective modes of the plasmonic nanostructure, the surface-enhanced CARS (SECARS)\(^{183,185-187}\) signal from molecules adsorbed onto the nanostructure will be further enhanced by the local fields of the excited plasmon modes. The electromagnetic enhancement factor in SECARS is given by

\[
G_{SECARS} = |E(\omega_P)/E_0(\omega_P)|^4 |E(\omega_S)/E_0(\omega_S)|^2 |E(\omega_{AS})/E_0(\omega_{AS})|^2 ,
\]

the product of the enhanced local electromagnetic fields at the characteristic frequencies of the spectroscopy: an appropriate plasmonic substrate for CARS would provide electromagnetic enhancements at these three characteristic frequencies.

In this chapter, we show that plasmonic nanostructures supporting Fano resonances can be designed to enhance the CARS with single-molecule sensitivity. Plasmonic Fano resonances by their nature as coupled subradiant and super radiant modes can provide much larger field enhancements than bright modes\(^{13,188-191}\). The substrate we use is a quadrumer, i.e., four coupled nanodisks (Figure 5.1b) that
possess a strong Fano resonance. The local fields give rise to a highly localized SECARS enhancement in a single junction at the center of the quadrumer structure, a field distribution particularly well suited for achieving single-molecule detection sensitivity. We verify SECARS of single molecules with Raman cross-sections as low as $10^{-30}$ cm$^2$ sr$^{-1}$, using a bi-analyte method.

5.2. Methods and instruments

5.2.1. SECARS substrate preparation

The quadrumeres were fabricated by standard positive-resist electron beam lithography by patterning a 50 or 25 nm thick Au on a 1 nm Ti adhesive layer, which had first been evaporated onto an ultra-smooth fused silica substrate (1 x 2 cm$^2$, surface finish 10/5, SVM). The diameters and gaps of the quadrumeres were determined by top-view SEM images, and heights were determined by 60° tilted-view SEM images (divided by $\cos 60^\circ$). The standard deviations (error bars) were calculated based on 20 quadrumeres. The fabricated quadrumeres were arranged in a 7 x 7 array with 6 μm intercluster distances to avoid coupling effects. The substrate was treated with an oxygen plasma (660 W, Fischione) for 250 sec for the removal of residual molecules prior to experimental use.

5.2.2. Dark-field scattering spectroscopy

Dark field scattering spectra were obtained by a custom-built microscope with 35° incidence from the substrate normal (Microscope: Axiovert 200 MAT,
Zeiss; Objective: 50×/0.55NA Epiplan-Neofluar, Zeiss; Spectrograph: SP2150, PI/Acton; CCD: PIXIS 400BR, PI/Acton).

5.2.3. Numerical simulation

Finite-difference-time-domain (FDTD) simulation commercial software (Lumerical FDTD Solutions 7.5.3) was used to obtain the near and far field properties of the quadrumer for normal incidence excitation. The top-view geometries were chosen to correspond as closely as possible to the experimentally obtained SEM images of the quadrumer structures, and the heights used in the simulations corresponded to the Au thickness deposited during sample fabrication. A 1.3 nm thick dielectric layer on the side and top surfaces of each disk was used to model the p-MA monolayer. The Johnson and Christy dielectric function\(^{193}\) was used for Au, \(\varepsilon_1 = 2.10\) for the infinite fused silica substrate, and \(\varepsilon_2 = 9\) for the p-MA molecules\(^{13}\). Charge density plots were obtained by calculating the difference of the normal component of the electric field above and below the Au surface (Gauss’s law).

5.2.4. Ensemble-molecule adsorption

The substrates were soaked in a 10 mM p-MA (4-Aminothiophenol, \(\text{H}_2\text{NC}_6\text{H}_4\text{SH}, 97\%, \text{Aldrich}\)) ethanolic solution, a 1 mM adenine (\(\text{C}_5\text{H}_5\text{N}_5, \geq 99\%, \\text{Sigma}\)) or benzocaine (\(\text{C}_9\text{H}_{11}\text{NO}_2, \text{Sigma}\)) aqueous solutions overnight. A monolayer of p-MA molecules are believed to self-assemble onto the Au quadrumer surface and to bind to the substrate via the strong Au-S bond. Adenine and benzocaine
molecules attach to the Au surface due to the Au-NH$_2$ bond. These substrates were then washed thoroughly to remove unattached molecules from the Au substrate prior to measurement.

5.2.5. Single-molecule deposition

25 mL of 200 nM p-MA ethanolic solution and 25 mL of 200 nM adenine aqueous solution were combined and mixed thoroughly. 10 μL of such mixture solution was drop-casted onto the SECARS substrate (1 × 2 cm$^2$), soaking the entire substrate surface and evaporating in ~ 2 sec, such that on average an estimated number of around 0.75 p-MA and 0.75 adenine molecules fell into each probe region (~ 250 nm$^2$ area) of the substrate. This substrate was dried in air overnight to immobilize the probe molecules on the substrate surface, then dried under nitrogen flow prior to the SECARS measurements.
5.3. SECARS substrates of Fano-resonant quadrumers

Figure 5.2 Experimental and FDTD simulated properties of the quadrumer with \( p \)-MA molecule monolayer coating. (a) Experimental (top) and calculated (bottom) linear scattering spectra of a single quadrumer before (black) and after (red) the \( p \)-MA absorption, obtained with horizontal polarization. The calculated spectra for both cases are consistent with their corresponding experimental results. Green dashed line: the pump beam (800 nm); red zone: the Stokes scattering region (848 \( \sim \) 952 nm); blue zone: the anti-Stokes scattering region (756 \( \sim \) 690 nm). The Stokes and anti-Stokes regions correspond to Raman shifts of 700 \( \sim \) 2000 cm\(^{-1}\). The inset shows a SEM image of a gold quadrumer. (b) Charge densities on the top surface of the quadrumer excited at 800 nm pump (top) and 900 nm Stokes (bottom), corresponding to the subradiant and superradiant modes, respectively.
(c) Field enhancement intensity ($g^2$) distribution at the anti-Stokes (left), pump (middle) and Stokes (right) frequencies for the $p$-MA 1070 cm$^{-1}$ mode evaluated at mid-height of the quadrumer. (d) SECARS enhancement ($G_{\text{SECARS}} = g_P^4 g_S^2 g_{\text{AS}}^2$) map for the mode in c. The maximum enhancement factor is $\sim 1.5 \times 10^{10}$ in the central gap, and significantly lower ($\sim 2.5 \times 10^6$) in the four peripheral gaps. All scale bars are 100 nm.

The plasmonic quadrumer$^{192}$ (Figure 5.2a, inset) is composed of four Au disks of diameter $158.9 \pm 2.2$ nm and height $51.1 \pm 2.5$ nm with an interparticle spacing of $15.4 \pm 1.1$ nm, evaporated onto a fused silica substrate (see Methods). The optical spectrum of a plasmonic quadrumer cluster clearly shows a strong Fano resonance due to its coupled subradiant and superradiant plasmon modes (Figure 5.2a). Its linear (Rayleigh) scattering spectrum (Figure 5.2a) reveals a narrow minimum centered at $\sim 772$ nm on top of a far broader resonance, which redshifts to $\sim 800$ nm after functionalization of a monolayer of $\text{para}$-mercaptoaniline ($p$-MA) molecules. To exploit these spectral properties for SECARS, it is most advantageous to minimize losses at the pump wavelength while maximizing far-field coupling for the wavelength range of the anti-Stokes emission. The reduction of scattered light at frequencies corresponding to the Fano dip maximizes energy coupling into the structure at those frequencies (Figure 5.2a, wavelength marked in green). For the anti-Stokes output light, the superradiant shoulder of the optical spectrum acts as an antenna, maximizing the propagation of the anti-Stokes light to the far field (Figure 5.2a, blue wavelength band).

The nature and origin of the Fano resonance can be better understood by examining the surface charge densities at different wavelengths associated with this
resonance (Figure 5.2b). The Fano resonance is a result of interference between a subradiant mode and a superradiant mode. For the resonant frequency of the Fano dip, dipoles of the left and right nanodisks oscillate out of phase with the top and bottom disks in this symmetry-breaking quadrumer (Figure 5.2b, green), indicating a small net dipole moment and subradiant behavior. For the broad plasmon peak, the dipoles of all four disks oscillate in phase, indicating superradiant behavior (Figure 5.2b, red). The pronounced Fano dip in the otherwise superradiant scattering continuum indicates resonant energy storage at the frequencies corresponding to this feature.192

By optimizing the nanodisk diameters and gap sizes, we can tune the plasmonic quadrumer geometry so that its Fano resonance corresponds to the frequency of the pump laser; then the superradiant shoulders to the red and blue of the Fano minimum correspond to the Stokes and anti-Stokes scanning regions of the SECARS spectrum, respectively. These simultaneous resonances in the same spatial location result in a “mixed frequency coherent mode” as previously described on more complex plasmonic clusters.188

The field intensity distributions for the plasmonic quadrumer at the pump, Stokes, and anti-Stokes frequencies, for the 1070 cm\(^{-1}\) Raman mode of the adsorbate molecule \(p\)-MA, are shown in Figure 5.2c. The strong spatial localization at all three frequencies leads to a tightly confined “SECARS hot spot” in the center of the cluster with an \(\sim 250 \text{ nm}^2\) size (only \(\sim 0.31\%\) of the surface area of a quadrumer) (Figure 5.2d). With horizontally polarized excitation, the four peripheral gaps have a
SECARS enhancement ~ 6000 times weaker than the central gap, thus a large CARS polarization could be effectively induced only by molecules located in the region of this central gap.

Figure 5.3 FDTD calculated enhancement spectra and comparison to SERS map of the quadrumer. (a) Local field enhancement \( (g = |E(\omega)/E_0(\omega)|) \) spectrum evaluated in the central gap, 1 nm from the side surface of the left disk at mid-height. (b) SECARS (or SECSRS) enhancement \( (G_{\text{SECARS}} = g_P^4 g_S^2 g_{\text{AS}}^2) \) spectrum at the same position as in (a). (c) Spatial distribution of the SERS enhancement \( (G_{\text{SERS}} = g_P^2 g_S^2) \) for the \( p-\text{MA} -1070 \text{ cm}^{-1} \) mode evaluated at mid-height of the quadrumer. The maximum enhancement factor is ~ 2.5×10^5 in the central gap.

The field enhancement in the central hot spot of this quadrumer is strongly dependent on wavelength, with a maximum field enhancement of ~ 22 at ~ 800 nm (Figure 5.3a). The SECARS over CARS enhancement was calculated to be between 0.7 ~ 2.3 × 10^{10} for the Raman modes spanning the range of 700 ~ 2000 cm\(^{-1}\), such as 1.5 × 10^{10} for the 1070 cm\(^{-1}\) \( p-\text{MA} \) mode and ~ 0.9 × 10^{10} for the 1580 cm\(^{-1}\) \( p-\text{MA} \) mode (Figure 5.3b). Taking into consideration that CARS is usually much more sensitive than spontaneous Raman scattering\(^{183}\), SECARS on this quadrumer is more than 10 orders of magnitude stronger than spontaneous Raman scattering.

For the same structure, the electromagnetic SERS enhancement (over SpRS) using the same pump laser frequency was calculated. Figure 5.3c shows the spatial
distribution of the SERS enhancement for the -1070 cm⁻¹ mode. The peak SERS 
enhancement is ~ 2.5×10⁵ at the central gap. The higher enhancement factor in 
SECARS over SERS, \( G_{\text{SECARS}} / G_{\text{SERS}} = g_P^2 g_A s^2 \sim 6 \times 10^4 \), is due to its higher order 
power dependence due to the additional anti-Stokes plasmon resonance.

Figure 5.4 Control experiment of SECARS on a symmetric square quadrumer. 
(a) Calculated linear scattering spectra obtained with horizontal polarization before 
(black curve) and after (red curve) the p-MA chemisorption. Green dashed line: the 
pump beam; red zone: the Stokes beam; blue zone: the anti-Stokes scattering region. 
The inset shows the geometry of the symmetric quadrumer. All disk diameters are 
148 nm with 50 nm heights and 15 nm gaps. (b) Spatial distribution of the SECARS 
enhancement (\( G_{\text{SECARS}} = g_P^4 g_S^2 g_A s^2 \)) for the p-MA anti-Stokes mode at -1070 cm⁻¹ 
evaluated at mid-height. The maximum enhancement factor is ~ 7.5×10⁸ in the 
central gap.

It is useful to compare the SECARS enhancement (over CARS) of this Fano 
resonant cluster with another plasmonic but non-Fano structure: A symmetric 
square quadrumer (Figure 5.4, inset) is composed of four Au disks of diameter 134 
nm and height 50 nm with interparticle spacing 15 nm. It shows a broad plasmon 
scattering (Figure 5.4a) over a large spectral range including pump, Stokes and anti-
Stokes frequencies, thus it is resonant with all three frequencies. No subradiant 
mode would be excited for this symmetric structure, and therefore this structure
lacks the Fano resonance (interference between the subradiant and the superradiant modes). This symmetric quadrumer was calculated to have a SECARS enhancement of $7.5 \times 10^8$ over CARS for the -1070 cm$^{-1}$ mode (Figure 5.4b); additionally a nanovoid gold surface has a SECARS enhancement of $\sim 10^5$ over CARS when all frequencies coincide with its plasmon resonances. These values are much smaller compared to a $1.5 \times 10^{10}$ enhancement by a Fano-resonant asymmetric quadrumer (Figure 5.2d).

### 5.4. Design of SECARS Experiment

![Figure 5.5 Schematic of the SECARS microscope.](image)

**Figure 5.5 Schematic of the SECARS microscope.** BS: beam splitter; PCF: photonic crystal fiber; $\lambda/2$: half-wave plate; DM: dichroic mirror; LPF: long-pass filter; BPF: band-pass filter; SPF: short-pass filter.

A sample-scanning nonlinear optical microscope was constructed for the
single-particle SECARS measurements, as shown in Figure 5.5. An ultrafast Ti:Sapphire laser (Mira 900, Coherent Inc.) was used to generate the 800 nm pulses (repetition rate 76 MHz). After passing through a Faraday isolator (EOT Inc.) which allowed only one-way transmission of light, the laser beam was split into two paths. One path formed the pump beam at 800 nm with 5 nm FWHM by two band-pass filters (FB800-10, Thorlabs); the other path generated the Stokes beam at 830 ~ 1050 nm by a nonlinear photonic crystal fiber (FemtoWhite800, Crystal Fiber A/S) for the Vis-NIR supercontinuum and then passed through a long-pass filter (BLP01-830R-25, Semrock). For each path, the polarization was controlled by a half-wave plate (10RP52-2, Newport) and a linear polarizer (LPVIS100, Thorlabs), and the intensity was attenuated by a neutral density filter (NDL-25C-4, Thorlabs). These two beams were then superimposed spatially using a dichroic mirror (DMSP805, Thorlabs). A motorized linear stage (ILS200CHA, Newport) was inserted into the Stokes path to overlap the pulses in time (pulse durations: pump ~ 200 fs; Stokes ~ 500 fs). The two horizontally polarized, collinear and coherent beams were then focused to ~ 1 μm diameter on an individual quadrumer using a 50× / 0.8NA objective (HC PL FLUOTAR, Leica), where both incident beams behave like normal-incident plane waves on the quadrumer surface\textsuperscript{188}. Substrates were mounted on a three-axis piezoelectric stage (P-545.3R2 NanoXYZ, Physik Instrumente (PI) GmbH) to position the desired quadrumer precisely at the beam focus.

The SECARS signal from the molecules was collected by a 60X / 0.7NA microscope objective with a variable coverslip correction collar (LUCPlanFL N, Olympus), then transmitted through a pair of short-pass filters (FF01-775/SP-25
and SP01-785RU-25, Semrock) to remove the excitation light. The light was focused onto the entrance slit of a spectrograph (SpectraPro 400i, PI/Acton) by an $f= 40$ mm cemented achromatic doublet lens (AC254-040-A, Thorlabs), and detected by a Si CCD array (PIXIS 100, PI/Acton). The SECARS polarization was analyzed by an additional polarizer (LPUV100, Thorlabs). A pair of CCD cameras (Guppy F-146, AVT and UI-2230-C-HQ, IDS) was used to obtain images of the back-scattered and transmitted light to assist in locating the specific quadrumer of interest on the substrate. When the CARS polarizations are generated in a volume much smaller than its propagation wavelength, and/or in the focused laser fields, the phase matching requirements for nonlinear optics can be fulfilled automatically ($|\Delta k \cdot z | << \pi \text{ when } z << \lambda$)\textsuperscript{181,194}.

Typically, SECARS experiments were performed with a total power of $40 \sim 100$ $\mu$W for ensemble molecules or $600 \mu$W for single molecules, corresponding to a power density of $4 \sim 10$ kW cm$^{-2}$ or $60$ kW cm$^{-2}$ (peak power density $0.13 \sim 0.325$ GW cm$^{-2}$ or $1.95$ GW cm$^{-2}$). Powers in both cases are smaller than those used in typical SERS experiments ($> 100$ kW cm$^{-2}$), but are capable of taking a full SECARS spectrum (-700 $\sim$ -2000 cm$^{-1}$) within a short time ($< 1$ sec), which were relatively stable during a long time ($\sim 10$ min).
Figure 5.6 (a) Input spectra of the pump (green) and Stokes (red) beams. (b) Example output signal of $p$-MA obtained with $P_P = 33 \, \mu W$ and $P_S = 67 \, \mu W$. The numbers of photons were recorded with pixel size $\sim 0.4$ nm.

The input (Figure 5.6a) consisted of a pump beam centered at $\omega_P = 800$ nm, and a Stokes continuum $\omega_S = 830 \sim 1050$ nm spanning several hundred nanometers to the long wavelength side of the pump wavelength. The resulting spectrum (Figure 5.6b) usually consists of several sharp anti-Stokes features on top of a broadband background. The background has two main contributions: a dominant two-photon luminescence (TPL) signal\textsuperscript{195,196}, as well as a much weaker FWM signal\textsuperscript{188}, both due to the Au nanostructure (Figure 5.7).
Figure 5.7 Example background signal obtained when both beams are applied to the pristine quadrumer. (a) the dominating TPL signal at a relatively lower laser power ($P_\text{P} = 33 \, \mu\text{W}$, $P_\text{S} = 67 \, \mu\text{W}$). (b) the FWM signal becomes obvious at a relatively higher laser power ($P_\text{P} = 0.5 \, \text{mW}$, $P_\text{S} = 1.0 \, \text{mW}$). SHG: second harmonic generation.

For detecting ensemble molecules, the applied laser power was usually less than 100 $\mu\text{W}$. When a pristine quadrumer was excited at this laser power level, a dominating TPL could be observed (Figure 5.7a). This spectrum was nearly identical to when the Stokes beam was removed. The TPL is independent of the molecular vibrations and is believed to be due to radiative recombination between Fermi level electrons and $d$-band photoexcited holes\textsuperscript{197,198}.

For detecting single molecules, the overall applied laser power was 600 $\mu\text{W}$. At this relatively higher power, the third order nonlinear process of FWM from Au quadrumer became not ignorable and need to be removed for data processing. Figure 5.7b show a typical FWM signal (on top of TPL) at a high excitation power of 1.5 mW.

The quadrumer is an optimized structure for improving the signal-to-background ratio: The SECARS background, originating from the Au metal, is mainly a function of the nonlinear susceptibility of Au, and also proportional to the amount of Au present in the probe region of the enhanced electromagnetic field\textsuperscript{187}. Although the quadrumer itself is relatively large, the background TPL and FWM are dominated by Au in the “hot spot” only, which is greatly reduced to a small region in the center of the structure due to the spatial distribution of the local field.
For the SECARS experiments, the background of TPL and FWM were measured prior on a pristine quadrumer sample. The output spectra were averaged at three different pump-Stokes delays (Figure 5.8), corrected (subtracting) for background noise (Figure 5.7), and calibrated (divided) by the quadrumer SECARS enhancement\textsuperscript{199} (Figure 5.3b) and instrument efficiency spectrum at each wavelength. The obtained spectra in wavelengths ($\lambda$) were then converted into wavenumbers ($k$) by the following equation:

$$\Delta k = 10^7 \times \left( \frac{1}{800} - \frac{1}{\lambda} \right)$$  \hspace{1cm} (5.3)

The reconstructed SECARS spectra were shown in the following sections.

The reason for averaging spectra at different pump-Stokes delays is: The pump pulse (duration $\sim 200$ fs) temporally overlaps only part of the Stokes pulse (duration $\sim 500$ fs) well, due to the complex temporal structure of the continuum Stokes pulses\textsuperscript{24}. To capture the full spectrum, we need to adjust the pump-Stokes delays, which results in the change of relative peak heights in different spectra (Figure 5.8). For the specific nonlinear PCF we used, the shorter wavelength component of the Stokes beam propagates faster than the longer component in the range of 830 $\sim$ 1000 nm. When the pump-Stokes delay increases, first the longer and then the shorter wavelength parts of the Stokes beam overlap with the pump. Correspondingly the output anti-Stokes peaks with maximum amplitudes show up at longer wavelengths gradually. Note that, for different time-delays, the same peaks exist at nearly the same wavelengths. These three output spectra (Figure 5.8) were then averaged for the pump-Stokes overlapping.
Figure 5.8 Example output signals of p-MA obtained with variable time delays between pump and Stokes pulses: (a) -50 fs, (b) 0 fs and (c) 50 fs. In all cases, $P_P = 33 \, \mu W$ and $P_S = 67 \, \mu W$, and generate 3 peaks at same wavelengths but different amplitudes.

5.5. Ensemble-molecule detection

We first perform SECARS with this quadrumer structure on some ensemble molecules ($\sim 10^3$ molecules bound to the Au surfaces of the probe region of the quadrumer structure). As shown in Figure 5.9, all three investigated molecules are absorbing in the UV and clearly nonresonant at both NIR excitations (pump and Stokes): p-MA absorbs at $\sim 256$ nm; adenine absorbs at $\sim 260$ nm; and benzocaine absorbs at $\sim 286$ nm.
Figure 5.9 Example Absorbance spectra of $p$-MA, adenine and benzocaine molecules, obtained using a Cary 5000 UV-Vis-NIR spectrophotometer. $p$-MA was taken at 250 μM concentration (in ethanol); adenine was taken at 1 mM concentration (in water); and benzocaine was taken at 50 μM concentration (in water). Green dashed line: the pump laser (800 nm); red zone: the Stokes laser (830 ~ 1000 nm).

Figure 5.10a shows the reconstructed SECARS spectrum of $p$-MA, where the broad Raman peaks (~ 100 cm$^{-1}$) are mostly due to the spectral bandwidth of the pump (~ 5 nm). Two prominent $p$-MA modes due to the electromagnetic (EM) field enhancement$^{13}$, a peak at ~ -1800 cm$^{-1}$ due to the overtone of the ring mode$^{200}$, and a weak mode at ~ 1290 cm$^{-1}$ possibly due to the combined contribution of CT (charge-transfer between Au surface and adsorbed molecules) and EM mechanisms can be observed. Interestingly, the CARS spectrum of $p$-MA showed quadrumer-to-quadrumer variations, characteristic of a depolarization behavior with random fluctuations, likely due to variable orientations of molecules within the gap$^{201,202}$.

Figure 5.10 SECARS experiments of ensemble molecules of $p$-MA on the quadrumer. (a) Reconstructed SECARS spectrum vs. Raman shift of $p$-MA shows two prominent peaks at -1070 cm$^{-1}$ (1) and -1580 cm$^{-1}$ (3), a weak charge-transfer mode at ~ -1290 cm$^{-1}$ (2) and an overtone of ring mode at ~ -1800 cm$^{-1}$ (4), all
corresponding to peaks with same numbers in Figure 5.6b. (b) Normalized peak power at -1070 cm$^{-1}$ vs. normalized total input $P_{\text{tot}}$ (black squares, $P_{\text{tot}} = 40 \sim 100$ μW with $P_1:P_2 = 1:2$), $P_P$ change only (orange circles, $P_P = 13 \sim 33$ μW with $P_S =67$ μW) and $P_S$ change only (cyan triangles, $P_S = 27 \sim 67$ μW with $P_P = 33$ μW) on a log-log scale. $P_S$ represents the overall power of continuum wavelengths. Dashed lines are linear fitting functions. Error bars represent standard deviations of $p$-MA CARS signals on five individual quadrumers.

The intensity of the -1070 cm$^{-1}$ $p$-MA mode (Figure 5.10b) was observed to depend cubically on the total input power $P_{\text{tot}}$, quadratically on the pump power $P_P$, and linearly with Stokes power $P_S$. These results follow the third-order nonlinearity scaling of equation 5.1, further confirming the CARS origin of the spectrum, and demonstrate that the intensities in our experiment have not reached the coherent-Raman saturation threshold$^{203}$.

Figure 5.11 SECARS experiments of ensemble molecules. (a) SECARS spectrum of adenine shows four expected peaks at -740 cm$^{-1}$ (1), -950 cm$^{-1}$ (2), -1270 cm$^{-1}$ (3) and -1450 m$^{-1}$ (4). (b) SECARS spectrum of benzocaine shows five expected peaks at -850 cm$^{-1}$ (1), -1160 cm$^{-1}$ (2), -1290 cm$^{-1}$ (3), -1610 cm$^{-1}$ (4) and -1700 cm$^{-1}$ (5).

Using this approach, we were able to obtain SECARS spectra from a variety of
other small molecules. The SECARS spectrum of adenine, one of the constituent bases of DNA and RNA, is dominated by the -740 cm\(^{-1}\) ring-breathing mode\(^{204}\) (Figure 5.11a). Benzocaine, another polyheterocyclic aromatic molecule, has a SECARS spectrum (Figure 5.11b) characterized by five primary modes\(^{205}\). The clearly resolvable features of these SECARS spectra indicate the potential for vibrational spectroscopy of these and similar molecular species in ultra-small quantities.

![Figure 5.12 SERS spectra of molecules absorbed on the nanoquadrumer surfaces, and normal Raman spectra of molecules in the solid state. (a) p-MA molecules, (b) adenine molecules. The same Raman modes are labeled with the same numbers as in Figure 5.10a and Figure 5.11a.](image)

For comparisons, we had measured SERS and normal Raman spectra of p-MA and adenine (Figure 5.12). They were acquired on a Raman microscope (Renishaw inVia, U.K.) with 785 nm excitation wavelength and 1.57 mW laser power at the
samples. Backscattered light was collected using a 50× / 0.75NA objective (N PLAN, Leica) with a 40 s integration time. SERS substrates and samples were prepared by the same method as for SECARS measurements of ensemble molecules.

As shown in Figure 5.12, we could observe some changes in peak positions, peak numbers and relative intensities of Raman modes when molecules are adsorbed on metal surfaces. This is due to the modification of molecule symmetry and corresponding differences in mode selection rules when the molecules are adsorbed to a surface\textsuperscript{206}. Compared with their normal Raman spectra (Figure 5.12, red), there are additional weak peaks for both p-MA and adenine in the SERS (Figure 5.12, blue) and SECARS (Figure 5.10a, Figure 5.11a) spectra. These additional modes could be due to the combined contribution of CT (charge transfer) and EM (electromagnetic) mechanisms; the former is a resonant Raman-like process serving as the intermediate stage (affinity level) for the Raman scattering\textsuperscript{207-210} in the SERS and SECARS. See Table 5.1, Table 5.2 and Table 5.3 for the complete Raman mode assignments of three analyst molecules.

The enhancement of surface Raman thus could have three contributions: resonant absorption of the molecule, CT from molecule to metal, and vice versa\textsuperscript{207,211}. Vis/NIR lasers may resonantly excite the molecule onto the affinity level in a CT process. Especially in low-concentration situations as in the following section of single-molecule experiments, molecules may lie flat on the Au surface, thus there is good coupling of molecules to Au by $\pi$-orbitals. The correspondingly
large vibronic mixing between the wave functions of molecule and metal can highly enhance the CT process\textsuperscript{211}.

For \textit{p}-MA molecules, the pump laser could produce the resonant transfer of electrons from the Fermi level ($E_f$) of the metal to the affinity (LUMO) level of adsorbed molecules; when the electron comes back to the metal, the molecules could remain vibrationally excited\textsuperscript{212}. Thus these molecule vibrations could be enhanced by the CT effect (b$_2$ CT modes in Table 5.1). Adenine molecules behave similarly to \textit{p}-MA in the CT process (~1340 cm\textsuperscript{-1} mode is identified as enhanced by the CT process\textsuperscript{213,214}; see Table 5.2).

**Table 5.1 – Assignments for the Raman bands of \textit{p}-MA molecules.** Modes enhanced by EM effect are labeled as $a_1$ totally symmetric modes, whereas modes enhanced by CT effect are labeled as $b_2$ non-totally symmetric modes. Reported results are based on normal Raman spectra measured on solid-state molecules.

<table>
<thead>
<tr>
<th>Measured SECARS</th>
<th>Measured SERS</th>
<th>Measured Raman</th>
<th>Reported\textsuperscript{207}</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>645 cm\textsuperscript{-1}</td>
<td>635 cm\textsuperscript{-1}</td>
<td>634 cm\textsuperscript{-1}</td>
<td>C-C-C bend ($a_1$)</td>
<td></td>
</tr>
<tr>
<td>828 cm\textsuperscript{-1}</td>
<td>823 cm\textsuperscript{-1}</td>
<td>820 cm\textsuperscript{-1}</td>
<td>C-H wagging ($b_1$)</td>
<td></td>
</tr>
<tr>
<td>1014 cm\textsuperscript{-1}</td>
<td>1008 cm\textsuperscript{-1}</td>
<td>1011 cm\textsuperscript{-1}</td>
<td>C-C bend; C-C-C bend ($a_1$)</td>
<td></td>
</tr>
<tr>
<td>-1070 cm\textsuperscript{-1}</td>
<td>1085 cm\textsuperscript{-1}</td>
<td>1087 cm\textsuperscript{-1}</td>
<td>1089 cm\textsuperscript{-1}</td>
<td>C-C bend ($a_1$)</td>
</tr>
<tr>
<td>1142 cm\textsuperscript{-1}</td>
<td></td>
<td>1142 cm\textsuperscript{-1}</td>
<td>C-H bend ($b_2$)</td>
<td></td>
</tr>
<tr>
<td>1185 cm\textsuperscript{-1}</td>
<td>1180 cm\textsuperscript{-1}</td>
<td>1173 cm\textsuperscript{-1}</td>
<td>C-H bend ($a_1$)</td>
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</tr>
<tr>
<td>-1310 cm\textsuperscript{-1}</td>
<td>1327 cm\textsuperscript{-1}</td>
<td></td>
<td>1310 cm\textsuperscript{-1}</td>
<td>C-C stretch; C-H bend ($b_2$)</td>
</tr>
<tr>
<td>1392 cm\textsuperscript{-1}</td>
<td></td>
<td>1403 cm\textsuperscript{-1}</td>
<td>C-H bend; C-C stretch ($b_2$)</td>
<td></td>
</tr>
<tr>
<td>-1460 cm\textsuperscript{-1}</td>
<td>1432 cm\textsuperscript{-1}</td>
<td></td>
<td>1445 cm\textsuperscript{-1}</td>
<td>C-C stretch; C-H bend ($b_2$)</td>
</tr>
<tr>
<td>1491 cm\textsuperscript{-1}</td>
<td>1496 cm\textsuperscript{-1}</td>
<td>1490 cm\textsuperscript{-1}</td>
<td>C-C stretch; C-H bend ($a_1$)</td>
<td></td>
</tr>
</tbody>
</table>
Table 5.2 – Assignments for the Raman bands of adenine molecules. Mode at 1340 cm\(^{-1}\) is enhanced by CT process. Reported results are based on normal Raman spectra measured on solid-state molecules.

<table>
<thead>
<tr>
<th>Measured SECARS</th>
<th>Measured SERS</th>
<th>Measured Raman</th>
<th>Reported(^{204})</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1580 cm(^{-1})</td>
<td>1592 cm(^{-1})</td>
<td>1597 cm(^{-1})</td>
<td>1595 cm(^{-1})</td>
<td>C-C stretch (a(_{1}))</td>
</tr>
<tr>
<td>-1800 cm(^{-1})</td>
<td></td>
<td>1795 cm(^{-1})</td>
<td></td>
<td>overtone of the ring mode</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 5.3 – Assignments for the Raman bands of benzocaine molecules. Reported results are based on normal Raman spectra measured on solid-state molecules.

<table>
<thead>
<tr>
<th>Measured SECARS</th>
<th>Reported(^{205})</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>-850 cm(^{-1})</td>
<td>861 cm(^{-1})</td>
<td>C-H stretch (out-of-plane)</td>
</tr>
<tr>
<td>-1160 cm(^{-1})</td>
<td>1171 cm(^{-1})</td>
<td>C-H bend (in-plane)</td>
</tr>
<tr>
<td>-1290 cm(^{-1})</td>
<td>1277 cm(^{-1})</td>
<td>C-N stretch; asymmetric C-O-C stretch</td>
</tr>
<tr>
<td>-1610 cm(^{-1})</td>
<td>1600 cm(^{-1})</td>
<td>C-C stretch</td>
</tr>
<tr>
<td>-1700 cm(^{-1})</td>
<td>1677 cm(^{-1})</td>
<td>C-O stretch</td>
</tr>
</tbody>
</table>
5.6. Single-molecule detection

We then examined whether SECARS obtained using this approach could achieve single molecule sensitivity for small molecules, which would require an enhancement factor of \( \sim 10^{10} - 10^{11} \). A polarization-sensitive CARS geometry (with a polarization analyzer oriented to transmit y-polarized light placed before the detector) was used to suppress \( \sim 99\% \) of the essentially x-polarized background FWM signal. The quadrumer dimensions slightly modified to reduce the unpolarized background TPL (Figure 5.13): The Au disks have diameter 157.2 \( \pm 1.84 \) nm and height 25.6 \( \pm 1.7 \) nm with interparticle spacing 15.3 \( \pm 1.22 \) nm. The Fano dip is centered at \( \sim 800 \) nm, compared to the \( \sim 772 \) nm Fano dip of the 50 nm thick quadrumer in detecting many molecules (Figure 5.2). This redshift is mostly due to the top and bottom surface charge interference in the thinner structure. When the Au volume (thickness) is reduced by half (25 nm thick compared to 50 nm thick), the background TPL generated by Au quadrumer is also reduced by half.

![Figure 5.13](https://example.com/f513.png)

**Figure 5.13** Properties of the quadrumer used for single-molecule measurements. (a) Experimental (black curve) and calculated (red curve) linear
scattering spectra of a single quadrumer obtained with horizontal polarization. Green dashed line: the pump beam; red zone: the Stokes scattering region; blue zone: the anti-Stokes scattering region. The inset shows a SEM image of a gold quadrumer (scale bar 100 nm). (b) SECARS (or SECSRS) enhancement ($G_{\text{SECARS}} = g_p^3 g_S^2 g_{\text{AS}}^2$) spectrum evaluated in the central gap, 1 nm from the side surface of the left disk at mid-height. It is between $0.6 \sim 1.5 \times 10^{10}$ for the Raman shift between 700 ~ 2000 cm$^{-1}$. It has a $\sim 1.0 \times 10^{10}$ enhancement for the $p$-MA 1070 cm$^{-1}$ mode, and a $\sim 1.4 \times 10^{10}$ enhancement for the adenine 740 cm$^{-1}$ mode.

To prove that we can observe SECARS signal from a single molecule, we used a bi-analyte method$^{172,175}$, where $p$-MA and adenine (both Raman cross-sections $\sim 10^{-30}$ cm$^2$ sr$^{-1}$ in air for NIR excitation$^{37,88}$) have clearly distinguishable Raman spectra allowing for the unequivocal identification of each molecule. A mixed solution of equal concentrations (100 nM) of the two molecules was drop-casted onto multiple (49) quadrumers for SECARS. This concentration was chosen to ensure that approximately 1.5 molecules fall into each probe region (250 nm$^2$ area) onto the substrate$^{172,175}$, based on our estimation. Each molecule type should have similar probability of deposition by the drop-casting method at this sufficiently low coverage, since two molecules will not compete for binding on the Au surface due to their very large separation. The binding affinities of these two analytes are measured by the adsorption isotherms as follows.
Figure 5.14 Properties Adsorption isotherms of (a) pure $p$-MA solutions, (b) pure adenine solutions, and (c) mixed 1:1 ratio solutions of $p$-MA and adenine. Dashed lines are the fitting of data points by Langmuir equations. Error bars represent the standard deviations from six individual quadruplers at each concentration. The $p$-MA intensities are based on the strong 1070 cm$^{-1}$ Raman mode, and the adenine intensities are based on the strong 740 cm$^{-1}$ Raman mode.

Figure 5.14 shows the absorption isotherms of pure molecule and mixed molecule (1:1 ratio) solutions at different concentrations. Instead of the drop-casting method used for single-molecule measurements (100 nM), the SECARS substrates were immersed into solutions with relatively higher concentrations (0.1 ~ 4 mM) overnight, and then washed very carefully to remove unattached molecules.

In the case of pure $p$-MA, the measured data points could be fitted by a Langmuir equation $\theta = 1.34P / (1 + 1.34P)$ with the Langmuir adsorption constant = 1.34, indicating a closed-packed analyte monolayer on the nanostructure surface for a high concentration solution. The absorption isotherm of pure adenine is similar to that of $p$-MA, indicating a similar behavior (Langmuir equation $\theta = 0.74P / (1 + 0.74P)$ with Langmuir adsorption constant = 0.74). In the case of mixed analytes, the
$p$-MA signals are stronger than adenine signals in the resulting spectra, especially at higher solution concentrations (> 1 mM). This indicates a competition between $p$-MA and adenine for adsorption onto the Au surface: $p$-MA has a much stronger affinity to the Au surface through a Sulfur-Au bond, compared to adenine with a Nitrogen-Au bond, thus $p$-MA has higher probability to form a layer on the surface, or it may slowly replace the attached adenine during overnight immersion. Note that, when the solution concentration reduces, signal intensity from $p$-MA and adenine are getting close, indicating less completion between these two molecules in lower concentrations (< 0.2 mM).

For the single-molecule measurements, we drop casted a very dilute (100 nM) bianalyte solution onto the substrate, where the solution will immediately evaporated in ~ 2 sec. All the drop-casted molecules will deposit onto the substrate, and the $p$-MA and adenine will not compete for the binding onto the Au surface due to their very large separation. Although the affinity of both pure molecules may be different, our method of drop-casting a 1:1 ratio mixed solution with extremely-low-concentration has a nearly equal chance of deposition.
Figure 5.15 Properties Four representative outputs of different single-molecule events obtained with $P_r = 200 \, \mu W$ and $P_s = 400 \, \mu W$ (average power density $60 \, kW \, cm^{-2}$). (a) pure $p$-MA, (b) pure adenine, (c) both and (d) none. The overlaid red circles highlight the single-molecule Raman signals on top of the background TPL, which cannot be completely removed by the polarizer.

Figure 5.15 shows typical single-molecule raw spectra for four different situations.

Figure 5.16 show 13 representative reconstructed single-molecule SECARS spectra. The major spectral features of $p$-MA is the -1070 and -1580 cm$^{-1}$ modes, and
adenine is the -740 cm\(^{-1}\) mode. The presence of either these features served as the discriminating factors in the analysis. Two sets of spectra correspond extremely closely to the \(p\)-MA and adenine SECARS spectra obtained using higher concentrations of each of those respective adsorbate molecules. The “mixed” spectra clearly have spectral features that correspond to the spectra of both molecules. At these concentrations, we observed good Raman-band reproducibility among quadrumers with fluctuations in intensities, frequencies and spectral features, most likely due to changing molecule symmetry depending on different molecular orientations attached to metal surfaces, different molecule orientations with respect to the analyzer and laser polarization, or various local environments. All these characteristics are believed to be signatures of single or a few molecules.
Figure 5.16 Reconstructed single-molecule SECARS spectra. (a) pure $p$-MA events, (b) pure adenine events and (c) mixed events.

In contrast to concentrated mixed solutions which should always yield mixed spectra, we observed that, for a series of 49 quadrumers, the SECARS spectra were dominated by either one analyte or the other, or no molecules detected at all (Figure 5.17): 20 showed no Raman signal, 14 showed pure $p$-MA feature, 12 showed pure adenine feature, and 3 showed mixed features from both analytes. At the extremely low concentration, the numbers of molecules in each probe region should follow the Poisson distribution$^{172,175}$.
\[ P(n) = e^{-\mu} \mu^n / n! \]  

Here \( n \) is the total number of molecules (\( p \)-MA or adenine) present in each probe region, and \( \mu \) is the expected value of \( n \). Here we assume all 3 mixed-feature events originate from one \( p \)-MA and one adenine, since the chance of three or more molecules in one probe region is much lower\(^{175}\). The probability of measuring either type of molecule should follow the binomial distribution. Thus, both the possibilities of two \( p \)-MA and two adenine are half of that of one \( p \)-MA and one adenine, then approximately 1.5 events of pure \( p \)-MA and 1.5 events of pure adenine should be due to two molecules of the same type. Thus there should be 12.5 events of a single \( p \)-MA and 10.5 events of a single adenine. We fitted these experimental values of \( P(0) = 20/49 \), \( P(1) = (12.5 + 10.5) / 49 \) and \( P(2) = (3 + 1.5 + 1.5) / 49 \) by the Poisson distribution using a commercial software (OriginPro 8.1, OriginLab), and obtained \( \mu = 0.89 \pm 0.24 \), close to our estimated value of 1.5. This value indicates a single-molecule level concentration in the sampled area.
Figure 5.17 Single-molecule SECARS detection of bialytes. (a) Three representative SECARS spectra showing a pure $p$-MA event (top), a pure adenine event (middle), and a mixed event (bottom). (b) Histogram of occurrences of none, pure $p$-MA, pure adenine and mixed molecules from one sampled array of 49 quadrumeres.

We can calculate the SECARS enhancement factor of this quadrumer by the single molecule SECARS measurements$^{211,216}$:
Here $I_{AS}$ is the SECARS signal intensity, $I_p$ is the pump intensity, $\sigma_{\text{Raman}}$ is the single molecule Raman scattering cross section, and Q is the collection efficiency. The detected signals integrated over the spectral bandwidth of $\sim 5$ nm (spectrometer pixel size $\sim 0.4$ nm) are $\sim 800$ counts/s for the -1070 cm$^{-1}$ p-MA and -740 cm$^{-1}$ adenine modes (Figure 5.15a and Figure 5.15b). The collection efficiency is $\sim 0.01$ due to a $\sim 0.14$ collection efficiency of the 0.7 NA objective, a $\sim 0.25$ transmission efficiency for the optics and a $\sim 0.5$ efficiency for the spectrometer ($\sim 0.7$ for the grating and $\sim 0.7$ quantum efficiency for CCD). Using $I_{AS} \sim 800 \ h \ c / \lambda \sim 2.15 \times 10^{-16}$ W, $I_p = 2 \times 10^4 \ W \ cm^2$, $\sigma_{\text{Raman}} \sim 10^{-30} \ cm^2/\text{sr} \sim 4\pi \times 10^{-30} \ cm^2 \sim 10^{-29} \ cm^2$, we calculated $\text{EF}_{\text{SECARS}}$ to be $\sim 10^{11}$ compared to spontaneous Raman scattering (SpRS) from the same molecule. This enhancement factor is several orders of magnitude larger than previously reported using the normal SECARS$^{183,184}$ or SERS$^{211,216-218}$ methods ($10^6 \sim 10^{10}$).

We can also estimate the size of the quadrumer probe region. When 10 $\mu$L of the mixed solution was drop coated onto the, it initially formed a very thin film (about 50 $\mu$m thick) of molecule solution on the 1 $\times$ 2 cm$^2$ substrate and then rapidly evaporated in $\sim 2$ sec, thus it can be approximated as a 2-dimentional film$^{217}$. The average surface density of the probe molecules is estimated to be $\sim 6,000$ per $\mu$m$^2$. Take the surface area of the quadrumer ($\sim 7.84 \times 10^{-2} \ \mu$m$^2$) into account, there should be $\sim 470$ molecules on each quadrumer. Since on average 0.89 molecule can be detected for each quadrumer, we estimated $\sim 0.19\%$ of the surface area of a
quadrumer (\(\sim 167 \, \text{nm}^2\)) has sufficiently large enhancement for SECARS, which is the strongly localized SECARS probe region (at the central gap of the quadrumer) and this value is close to the calculated result in Figure 5.2d. This estimation may be affected by the variation of surface density of molecules from the drop coating process, but is sufficient to demonstrate that only very small portion of the structure surface is “SECARS active”.

5.7. Conclusions

We have demonstrated SECARS utilizing a Fano resonant plasmonic quadrumer substrate, which provides a \(\sim 10^{11}\) enhancement over spontaneous Raman scattering, and is capable of single molecule sensitivity with Raman cross-sections \(\sigma_{\text{Raman}}\) as low as \(\sim 10^{-30} \, \text{cm}^2 \, \text{sr}^{-1}\). These values are among the smallest values for molecules (except perhaps for \(\text{N}_2\) and alkane molecules, which have \(\sigma_{\text{Raman}} \sim 10^{-31}\) and \(10^{-32} \, \text{cm}^2 \, \text{sr}^{-1}\), respectively, at NIR excitations\(^{88,219}\)). Obtaining single molecule spectra using a substrate that can be fabricated with standard lithographic methods can, in principle, ultimately open the door to the identification of unknown molecules at the ultimate limits of chemical sensitivity.

This new technique, as a fundamental scientific tool, could come in handy for a variety of fields. It could be used in any application that calls for a sensitive chemical composition analysis, such as non-invasively investigating archaeological materials, analyzing environmental pollutants and detecting pharmaceutical ingredients and extremely low concentrations of drugs in saliva. It could instantly diagnose some
disease biomarkers in just one drop of blood too and might accurately be able to
detect some explosives very quickly (within a second).

This SECARS technique may work in the further, as a molecular computer chip
or logic gate. This way of computing would actually involve some types of chemical
reaction, where we could distinguish the molecule types before and after the
reactions and 'count' the number of these molecules by their quantized optical
intensities. Such a molecular computing technique, relying on small molecules,
might prove much more powerful, and cheaper than today's silicon-based
computers.
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