Second and Third Harmonic Generation in CuS/Au/Al Nanohybrids

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Undergraduate Research Project

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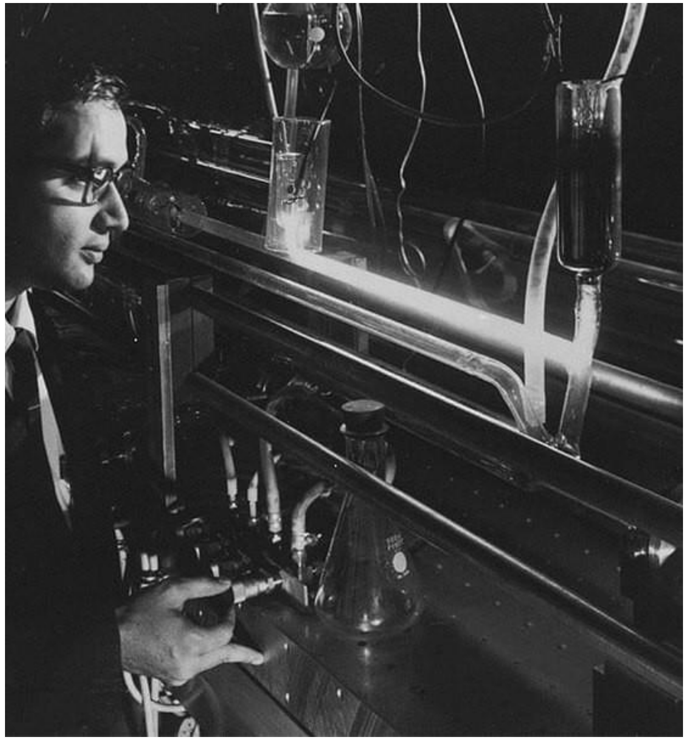
The Laser: Introducing Nonlinear Optics



- Incredibly coherent and intense beams of monochromatic light
- New phenomena unexplained by conventional optics

Theodore Maiman: first working laser (1960)

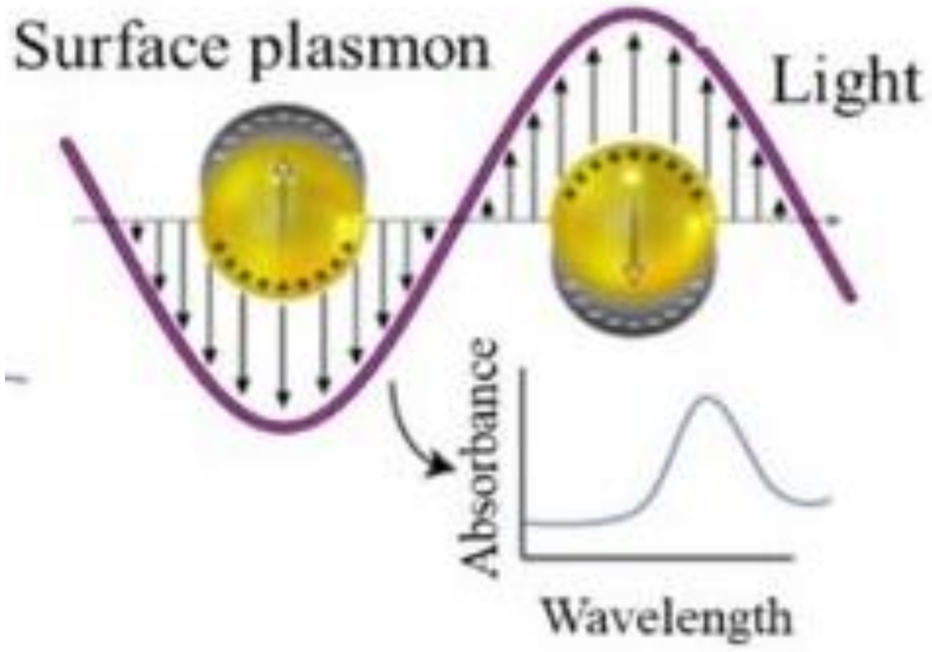
https://www.lasitlaser.com/laser-marking-history/

Frank et al. (1961): first observation of the **second harmonic** (arrow)

$$\vec{P} = \epsilon_0 \chi^{(1)} \vec{E} + \epsilon_0 \chi^{(2)} \overrightarrow{E^2} + \epsilon_0 \chi^{(3)} \overrightarrow{E^3} + \cdots$$

Why Metallic Nanoparticles?

- Surface plasmon polaritons
- Dipole-dipole interactions
  - Large local electric fields
  - Enhanced harmonic generation signal
- Applications:
  - Photothermal cancer therapy
  - Surface-enhanced Raman spectroscopy



Plasmon resonance

Source: Masson, 2020

Maxwell → Nonlinear Coupled Wave Equation

$$\nabla \cdot \vec{E} = 0 \qquad \nabla \cdot \vec{H} = 0$$

$$\nabla \times \vec{E} = -\mu_0 \frac{\partial \vec{H}}{\partial t} \qquad \nabla \times \vec{H} = \epsilon_0 \frac{\partial \vec{E}}{\partial t} + \frac{\partial \vec{P}}{\partial t}$$

- Plane wave approximation
- Nonlinear polarization

- Slowly-varying amplitude approximation

$$\frac{\partial A}{\partial z} = \frac{ik}{2\epsilon}\left(\hat{a}_0 \cdot \overrightarrow{P'}\right)e^{-i(kz-\omega t)} \qquad I = \frac{1}{2}c\epsilon_0 n|A|^2$$

Density Matrix → Susceptibility → Material Response

- Two-level system: $|\psi\rangle = c_1|1\rangle + c_2|2\rangle$
- Density matrix:

$$\begin{cases} \rho_{11} = c_1 c_1^* = |c_1|^2 \\ \rho_{12} = c_1 c_2^* \\ \rho_{21} = c_2 c_1^* = \rho_{12}^* \\ \rho_{22} = c_2 c_2^* = |c_2|^2 = 1 - \rho_{11} \end{cases}$$

➢ Schrodinger's Equation
➢ Perturbation Theory
➢ Decay of states
➢ Interaction Hamiltonian
➢ Steady-state approximation

→ Density matrix equations of motion

Solution to Nonlinear Coupled Wave Equation

$$A_2^m = \left(\frac{k_2 L}{2\epsilon_m(2\omega_p)}\right)\left(\frac{\mu_{21}^3}{\epsilon_0 V_m \hbar^2 \gamma_{21}^2}\right)\boxed{(\Lambda_{sd}^m)^4}\Xi_m^{(2)} A_p^2(0) F(\Delta k_2 L)$$

$$A_3^m = \left(\frac{k_3 L}{2\epsilon_m(3\omega_p)}\right)\left(\frac{\mu_{21}^3}{\epsilon_0 V_m \hbar^3 \gamma_{21}^3}\right)\boxed{(\Lambda_{sd}^m)^6}\Xi_m^{(3)} A_p^3(0) F(\Delta k_3 L)$$

Term: Total coupling constant: enhancement from surface plasmon polariton and dipole-dipole interaction

Solution to Nonlinear Coupled Wave Equation

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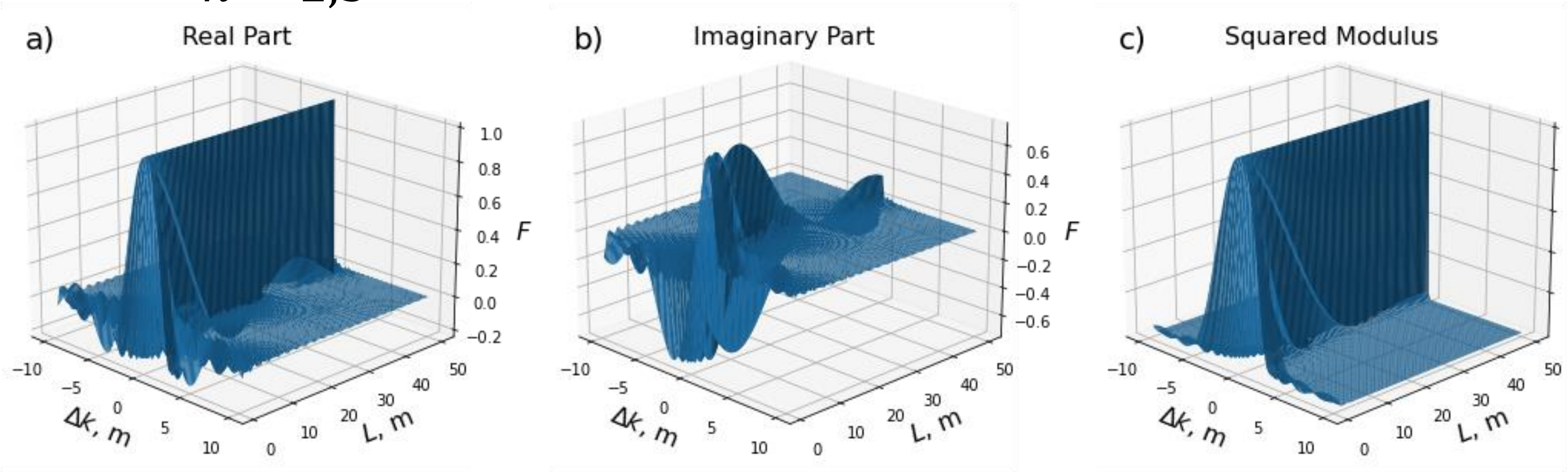
Term: phase factor (contains oscillatory behaviour)

Phase Matching Is Necessary!

$$\Delta k_n = nk_p - k_n$$
$$n = 2,3$$

Phase Mismatch Factor $F(\Delta kL)$

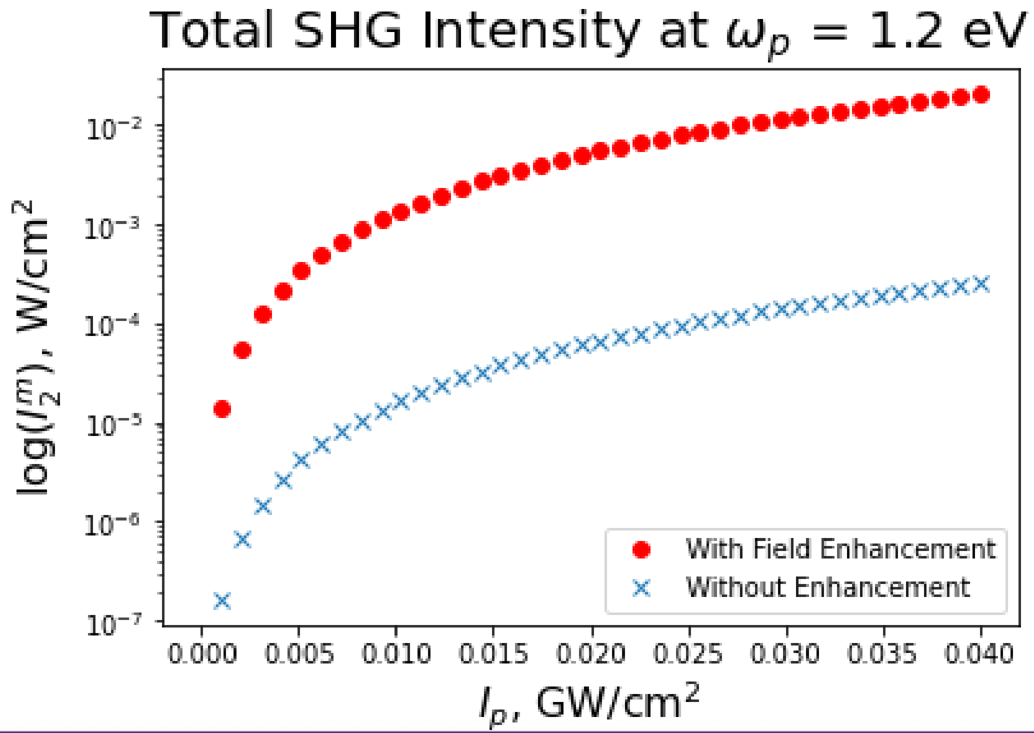


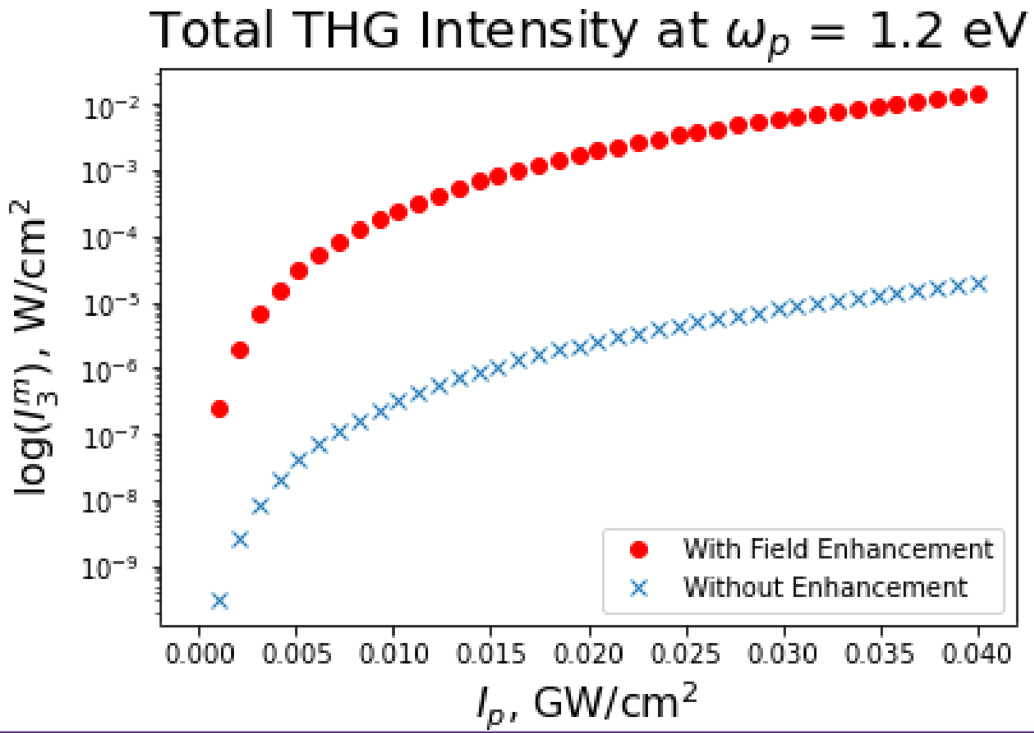
- If $\Delta k \neq 0$, wave **attenuates**
- For $0 \leq \omega_p \leq 10$ eV, $\frac{\Delta k}{k_p} \leq O(10^{-15}) \Rightarrow$ negligible attenuation

SPP and DDI provide up to 10^3-fold intensity enhancement

$$I_2^m = \alpha_2 (\Lambda_{sd}^m)^8 \left|\Xi_m^{(2)}\right|^2 I_p^2 \qquad I_3^m = \alpha_3 (\Lambda_{sd}^m)^{12} \left|\Xi_m^{(3)}\right|^2 I_p^3$$

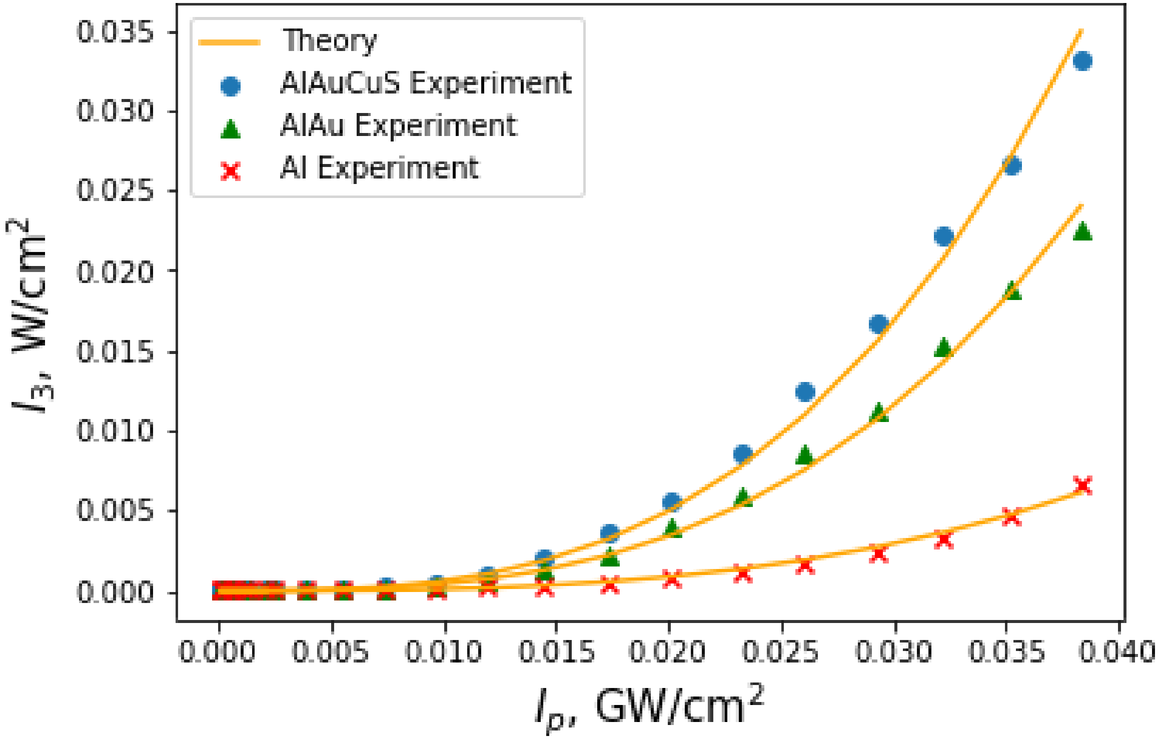
No enhancement: $\Lambda_{sd}^m = 1 + \Pi_{spp}^m + \Pi_{ddi}^{tot} \equiv 1$





Experimental Test: Vanderbilt Group

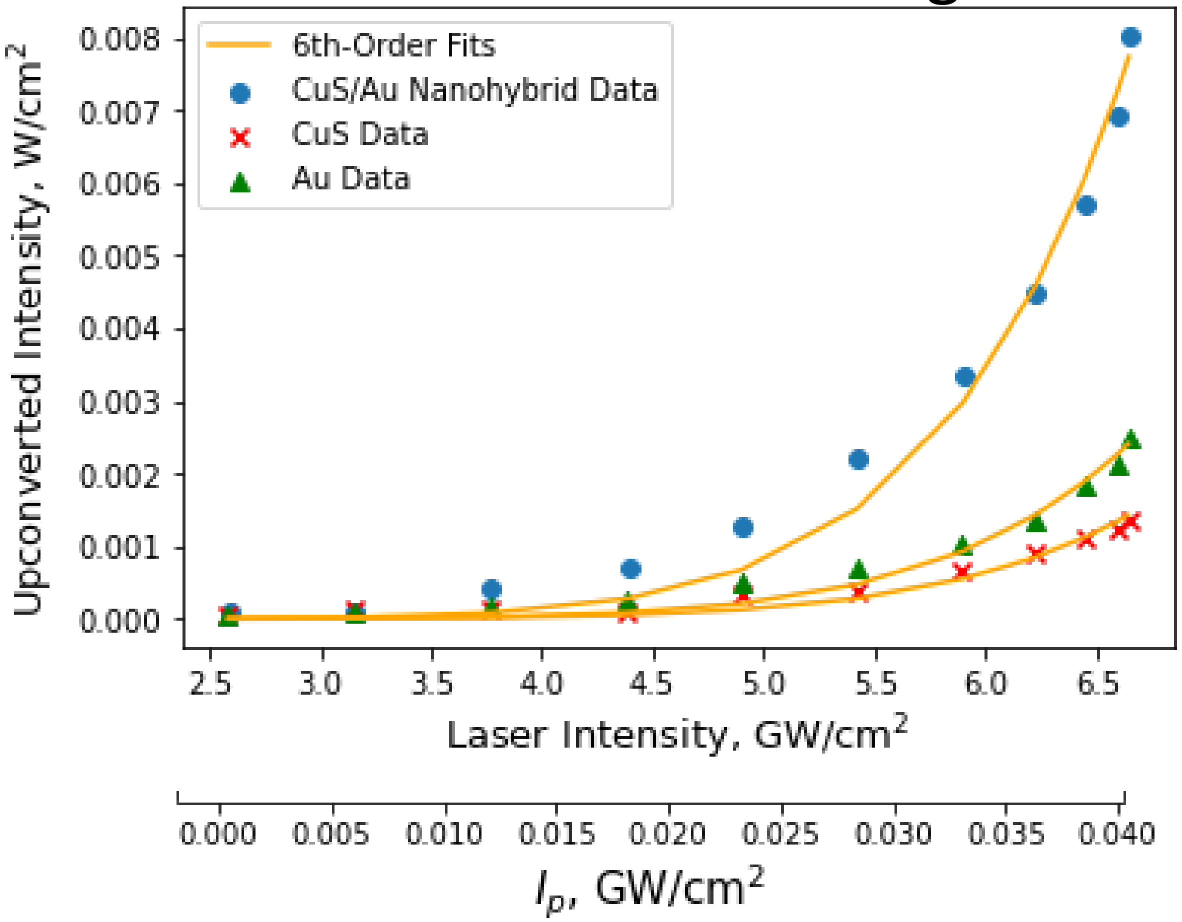
- THG in Al/Au/CuS nanohybrid



- ➢ DDI coupling constant as fitting parameter
- ➢ Chi-squared test: $p \approx 1$
- ➢ Theory and data agree

Experimental Test: Spear et al., 2020

Studied "second harmonic generation" in CuS/Au nanohybrids



Fit is 6th-order!

Our theory would predict a second-order relationship.

Why the discrepancy?

- Very high laser intensities in this experiment
- Higher-order phenomena likely at play

Conclusions

- ✓Equations derived for intensities of second and third harmonic generation signals from metallic nanohybrids
  - ✓Quadratic/cubic in incident intensity for SHG/THG
- ✓Phase-matching is required and met in these experiments
- ✓SPP and DDI effects allow for strong enhancement of optical signal
- ✓Use of multi-layer system allows for stronger signals

Thank you! Questions?