Enhancement of Harmonic Generation in Bilayer Au-CuS Nanoparticle Films

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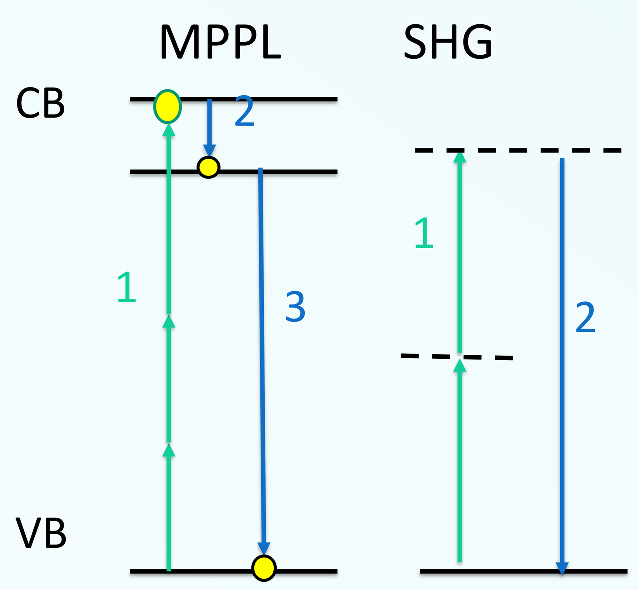
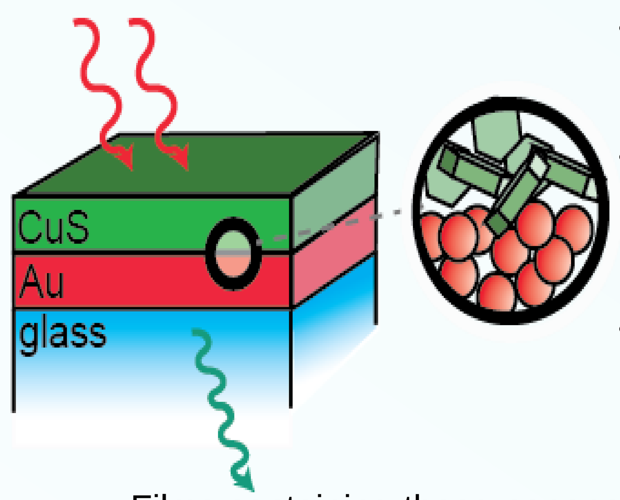
Introduction

- Second harmonic generation (SHG) is the sum frequency generation process by which two equivalent photons parametrically combine to form one photon. Third harmonic generation (THG) is the three photon equivalent
- Multiple-photon photoluminescence (MPPL) is a process in which multiple photons excite a valance band electron to the conduction band, producing an exciton. When the electron-hole recombination occurs, one photon is emitted.





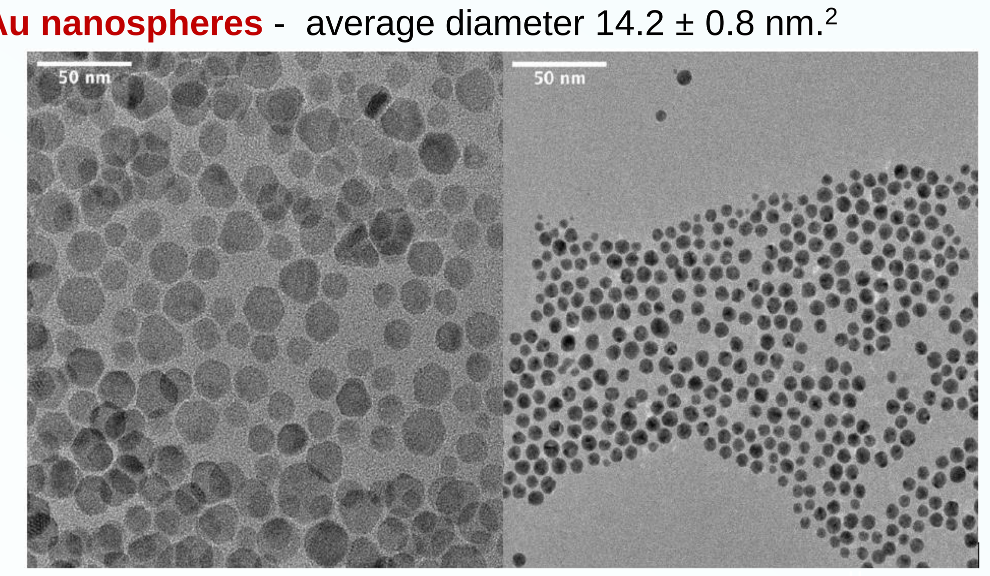
- Au and CuS (covellite) nanoparticles have plasmon resonances that are harmonically resonant($2\lambda_{Au,LSPR} = \lambda_{CuS,LSPR}$)
- Structuring these materials in close proximity produces an enhancement in SHG by the harmonic coupling of their plasmon resonances.
- By creating heterostructures containing both nanoparticles, generation of second harmonic greater than either nanoparticle alone was demonstrated.
- Films containing these nanoparticles, produced a facile bath method, exhibited high up-conversion efficiency, by both the SHG and MPPL mechanisms.

Nanoparticle Synthesis

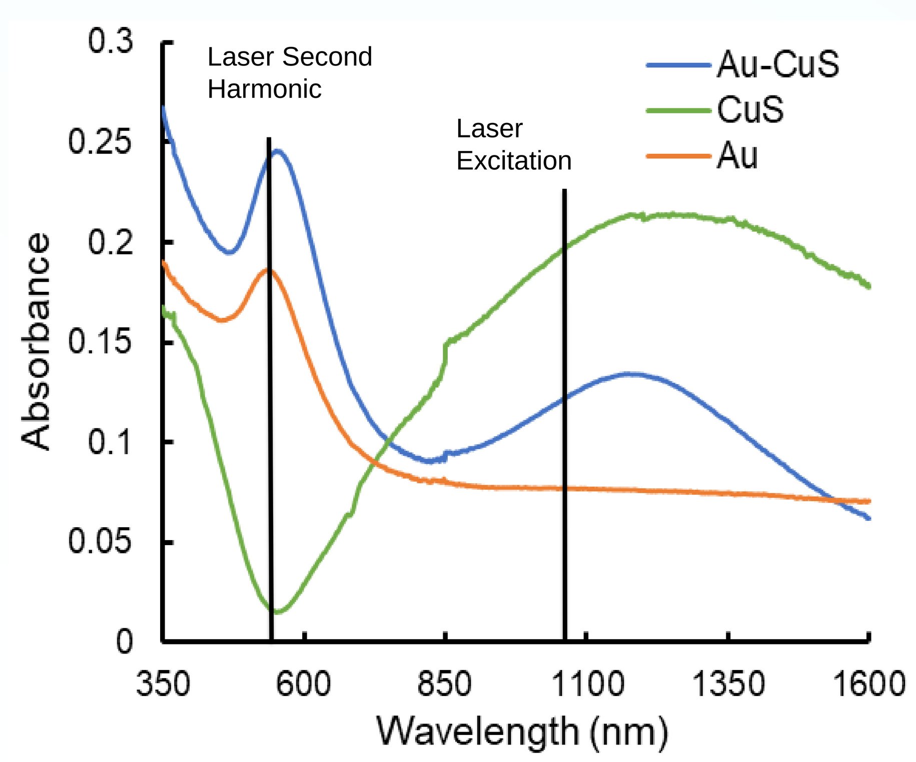
TEM images of as-synthesized nanoparticles:

CuS hexagonal nanodisks - average width 19 ± 3 nm, average thickness 4.9 ± 1.0 nm. [1]

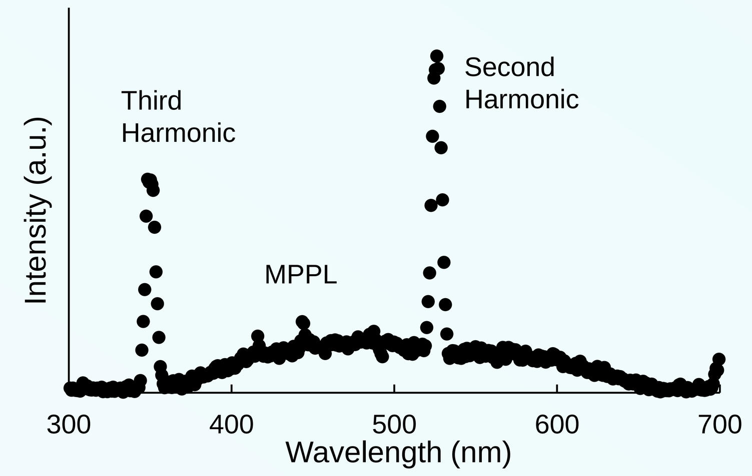
Au nanospheres - average diameter 14.2 ± 0.8 nm.[2]



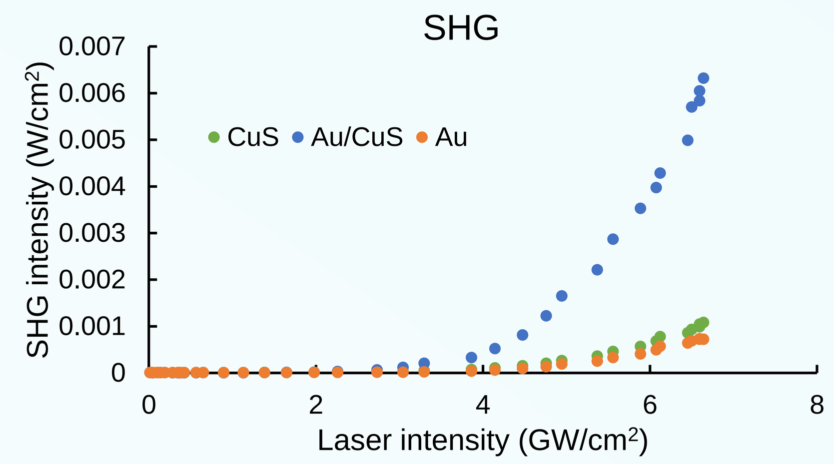
CuS **Au**

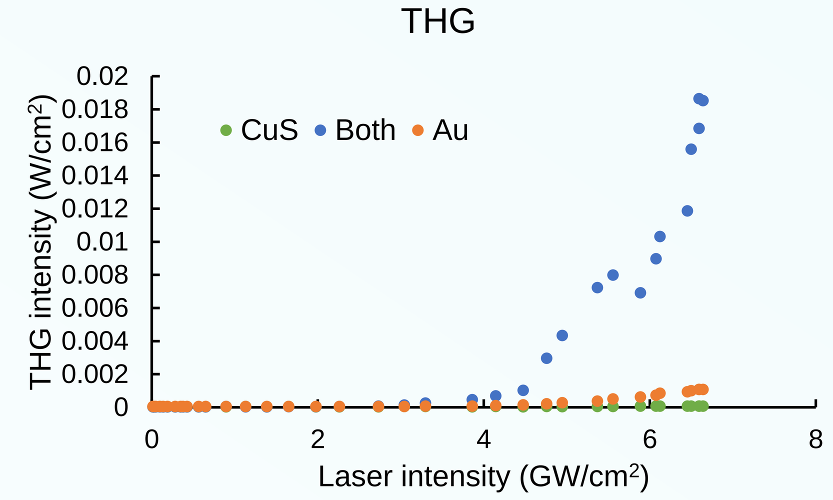


Harmonic generation results



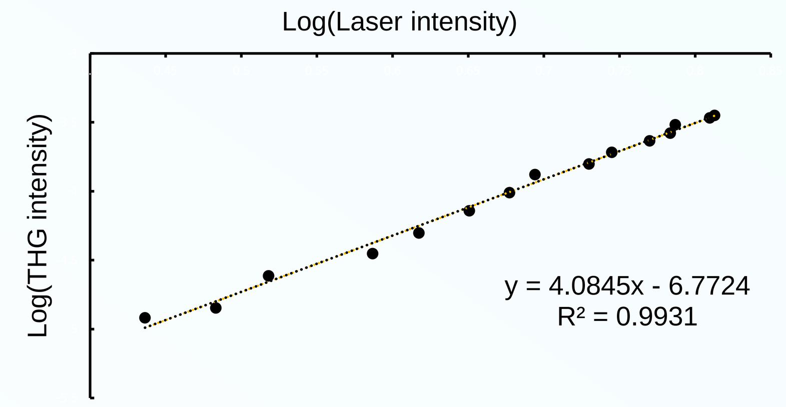
- Output of bilayer films showed multiple sources of upconversion
- Filtering was used to select parts of the output spectrum to isolate the SHG, THG, and MPPL effects
- Au/CuS films show unexpectedly high levels of 3rd harmonic generation (THG)
- Enhancement of THG proves more prominent than SHG
  - 7x increase in SHG
  - 20x increase in THG



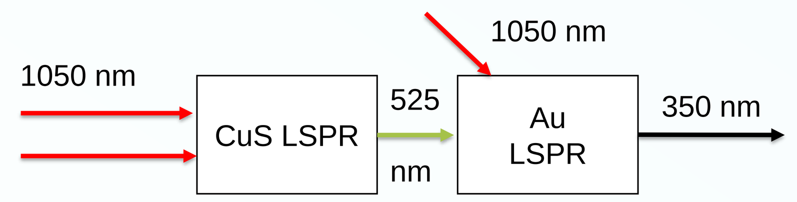


Y m*x^b

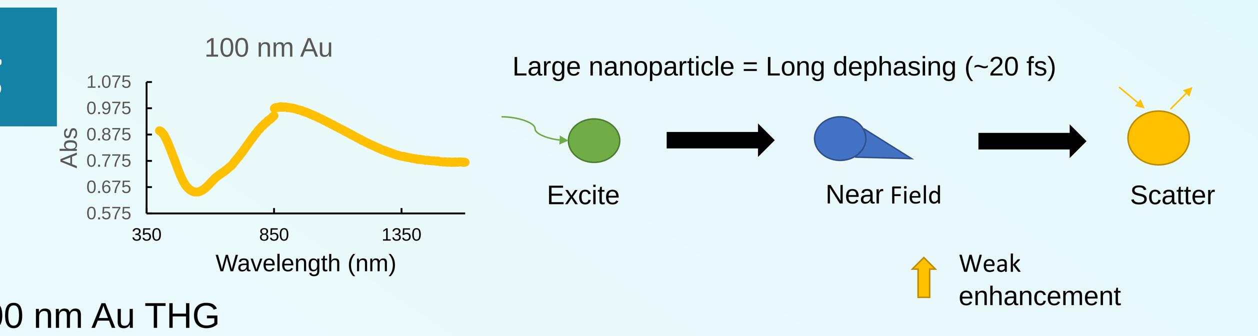
$Log(Y)=log(mx^b)=b*log(x)+blog(m)$

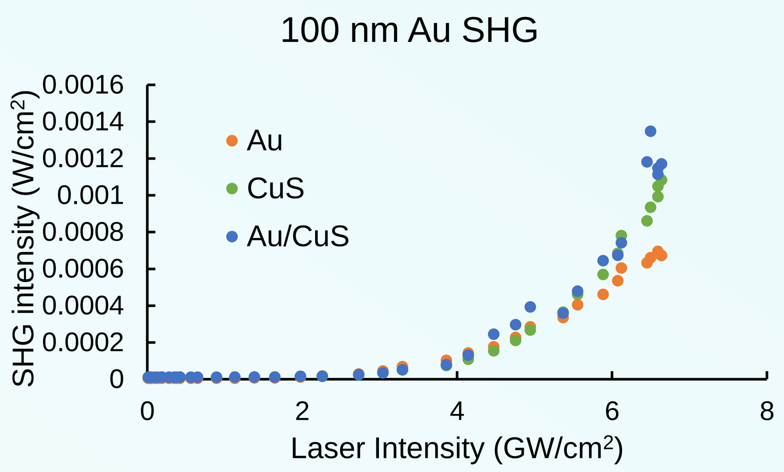


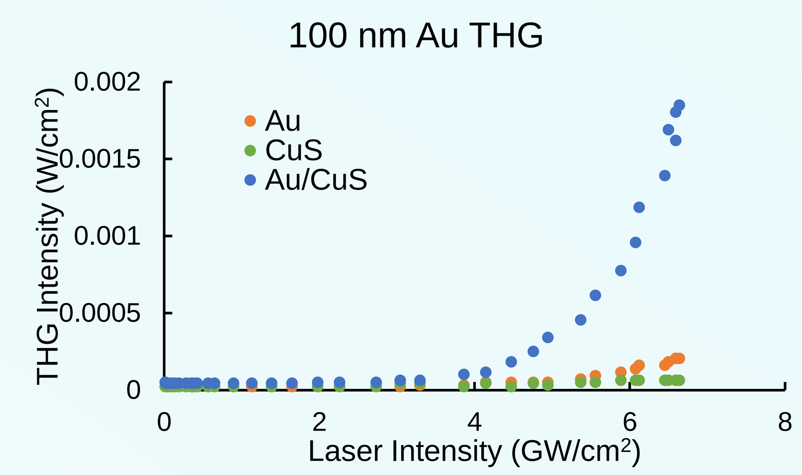
- In Au/CuS nanostructures, 3rd harmonic light is produced proportionally to 4th order of laser intensity
- How can 3ω light be produced in an even-order process?
- There is precedent for sum frequency generation as a route.[3]

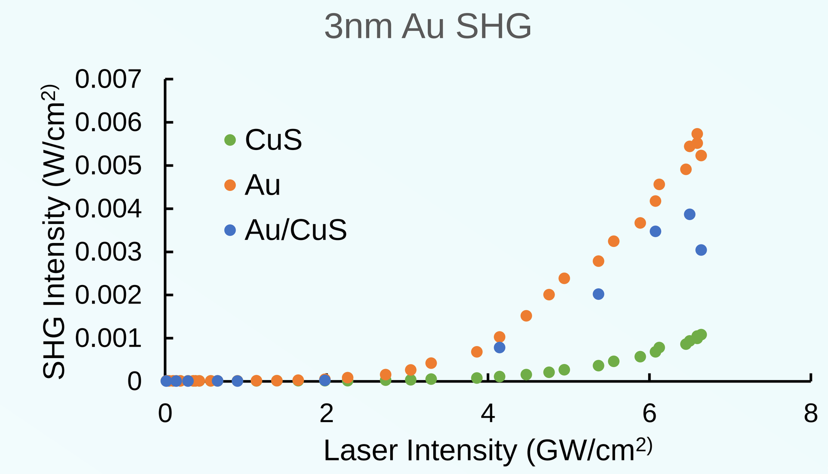


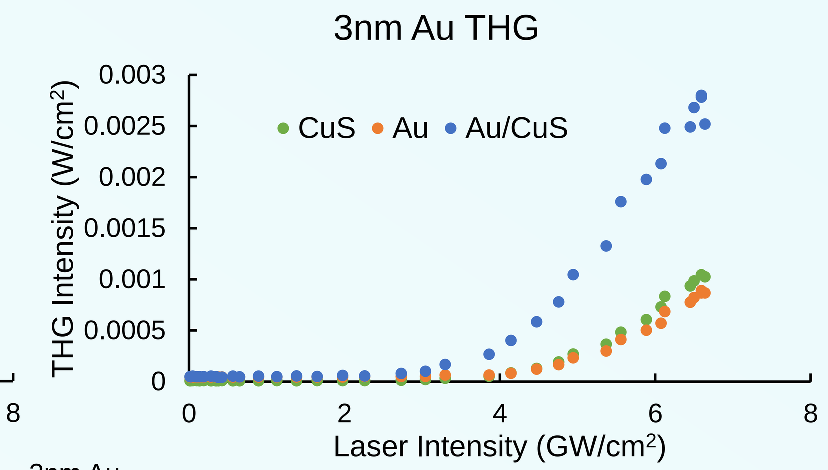
Size properties of Au plasmon coupling

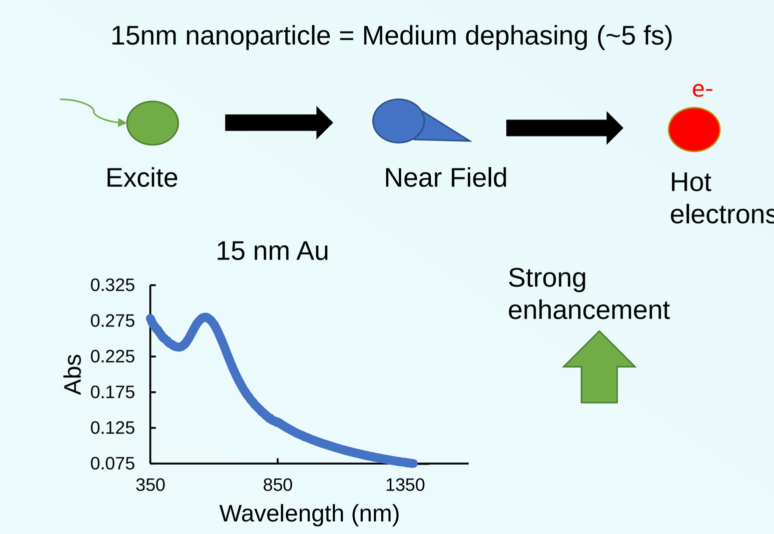


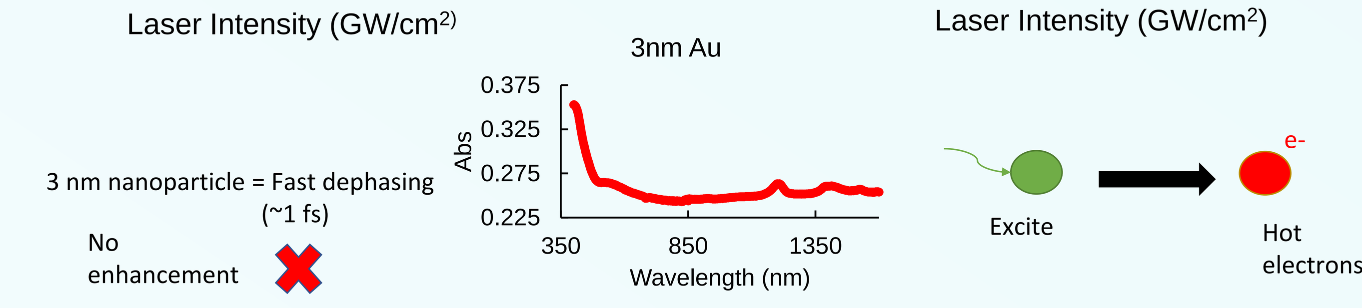






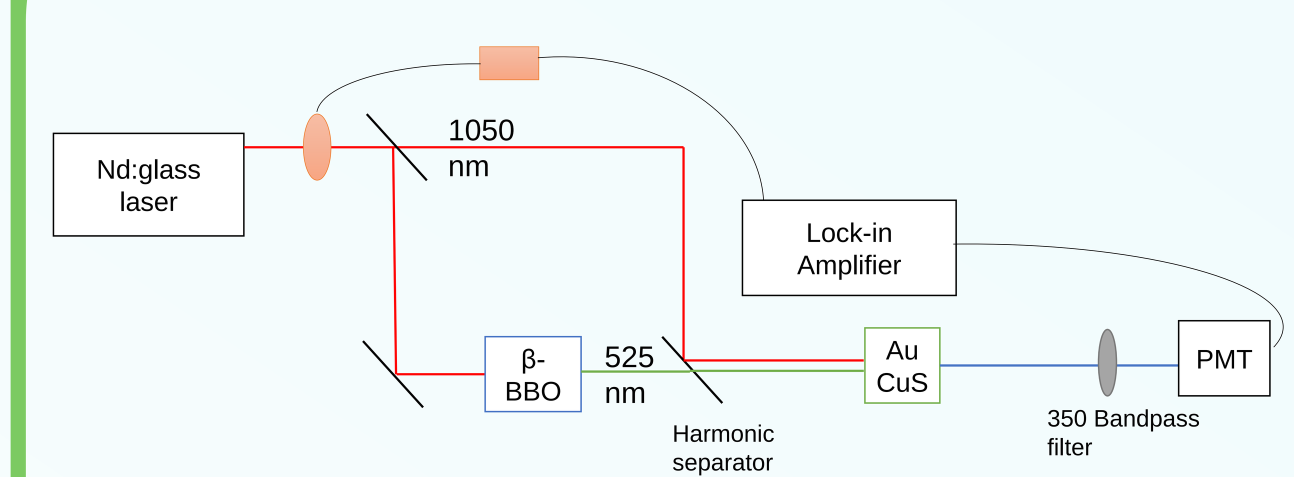




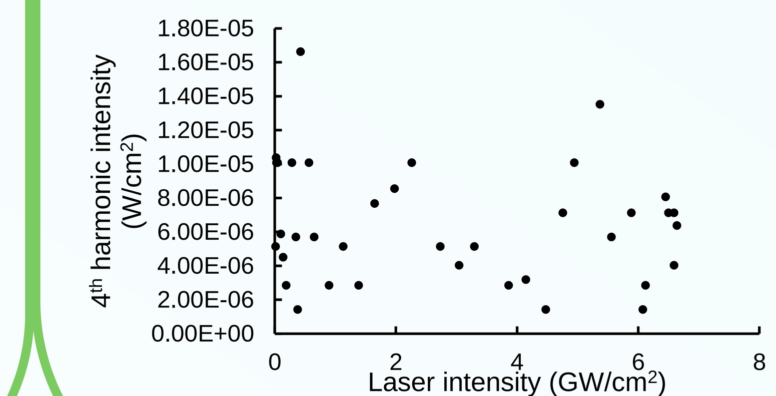


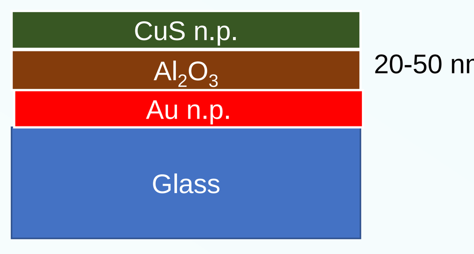
- Large Au nanoparticles produce no SHG enhancement & modest THG increases (8x).
- Middle size Au nanoparticles also exhibit the most SHG & THG enhancement (20x) (see data middle column).
- Small Au nanoparticles also do not exhibit any SHG enhancement & modest THG increases (2x).
- The lack of THG enhancement with detuned or quenched Au nanoparticle plasmon resonances indicates that harmonic pairing of the CuS and Au LSPR is the critical factor in the increased harmonic generation

Developing Research Directions



- Directly probe ω+2ω sum frequency generation properties of Au and CuS nanoparticles
- No measurable 4th Harmonic
- Examine dependence of THG enhancement on separation of Au & CuS nanoparticles
  - Adding Al_2O_3 layers of controlled thicknesses using Angstrom system to probe 10-100 nm range





Conclusion

- Au nanospheres have a plasmon resonance at the second harmonic of the fundamental plasmonic resonance of CuS nanoparticles.
- Third harmonic light generated with 4th order dependence on pump intensity
- Enhancement of harmonic generation is dependent on plasmonic properties.
- Metal-semiconductor plasmonic nanoparticle systems possess significant advantages over existing up-conversion materials including:
- Greater up-conversion efficiency per unit thickness than β-Barium Borate, a high-performance nonlinear crystal.
- Inexpensive and easily scalable synthesis and film deposition
- SHG and THG enhancement centered on the favored wavelength for dispersionless propagation in the telecommunications band
- No requirement for phase matching

Acknowledgements

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References:

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2) Xie, Y.; Carbone, L.; Nobile, C.; Grillo, V.; D'Agostino, S.; Della Sala, F.; Giannini, C.; Altamura, D.; Oelsner, C.; Kryschi, C.; et al. Metallic-like Stoichiometric Copper Sulfide Nanocrystals: Phase- and Shape-Selective Synthesis, near-Infrared Surface Plasmon Resonance Properties, and Their Modeling. *ACS Nano* **2013**, *7* (8), 7352–7369.
3) Zilli, A.; Rocco, D.; Finazzi, M.; Francescantonio, A.; Duo, L.; Gigli, C.; Marino, G.; Leo, G. De Angelis, C.; Celebrano, M. Frequency Tripling via Sum-Frequency Generation at the Nanoscale ACS Photonics 2021, 8, 4, 1175–1182
4) Li et. al.; Nature Photonics 2015, 9, 603