Enhancement of Third Harmonic Generation via harmonic plasmon coupling in Au/CuS nanoparticle films

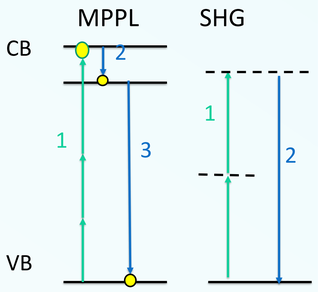
Nathan J. Spear[1], Yueming Yan[2], Richard F. Haglund[2], Janet E. Macdonald[3]

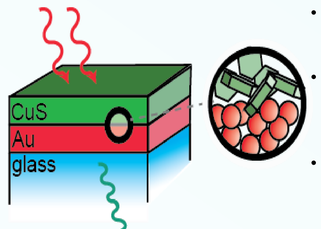
Interdisciplinary Materials Science[1], Department of Physics and Astronomy[2], and Department of Chemistry[3]

Vanderbilt University

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.



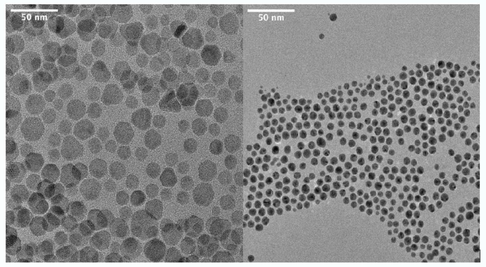


- Au and CuS (covellite) nanoparticles have plasmon resonances that are harmonically resonant($2\lambda_{Au,LSPR} = \lambda_{CuS,LSPR}$)
- Structuring these materials in close proximity produces an enhancement in SHG by the harmonic coupling of their plasmon resonances.
- By creating heterostructures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

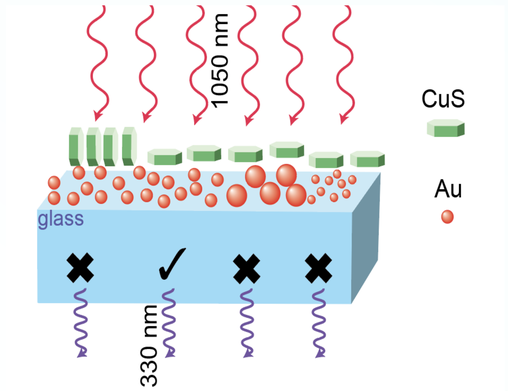
- Films containing these nanoparticles, produced a facile bath method, exhibited high up-conversion efficiency, by both the SHG and MPPL mechanisms.

Nanoparticle Synthesis

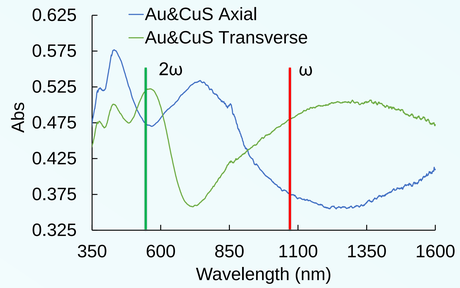
TEM images of as-synthesized nanoparticles:
CuS hexagonal nanodisks - average width 19 ± 3 nm, average thickness 4.9 ± 1.0 nm. [1]
Au nanospheres - average diameter 14.2 ± 0.8 nm.[2]
Spin coated onto glass to form bilayer films



CuS **Au**

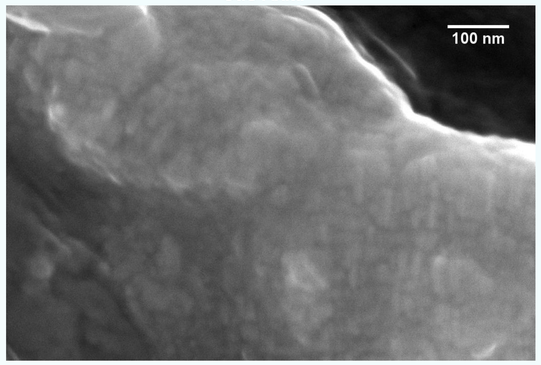


CuS Nanodisk Orientation

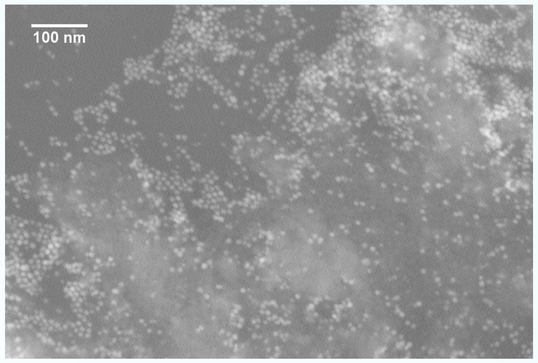


- Change in orientation of CuS nanoparticles caused shift in LSPR peak due to change in which mode was excited (in-plane vs out-of-plane)

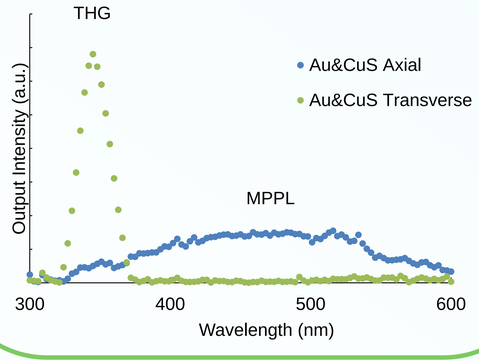
CuS Axial



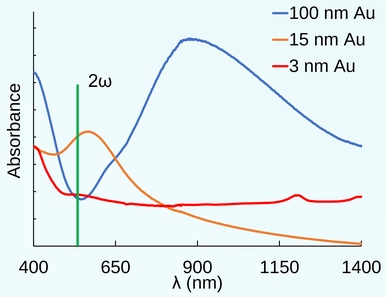
CuS Transverse

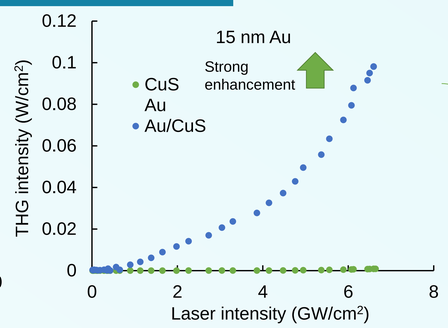


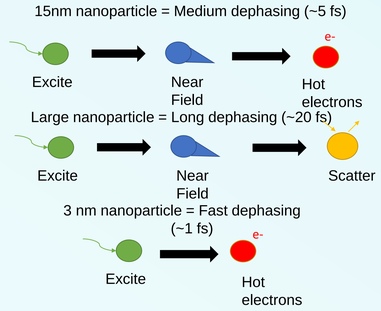
- Detuning of CuS LSPR from harmonic resonance condition causes shift in upconversion mechanism—from THG to MPPL.
- Separate resonances at ω & 2ω necessary for enhancement of THG

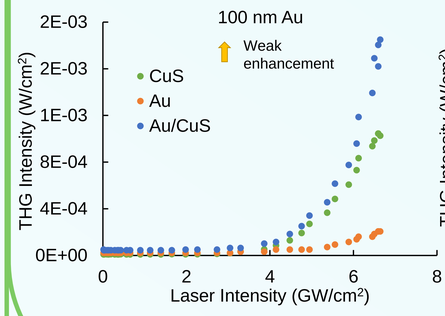


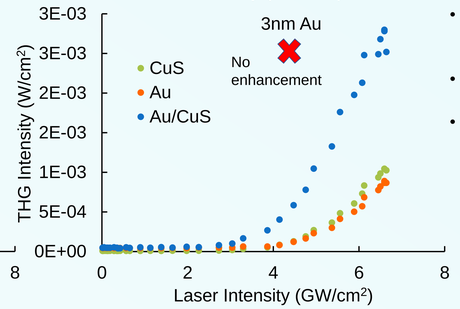
Au Nanoparticle Size Dependence







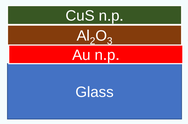




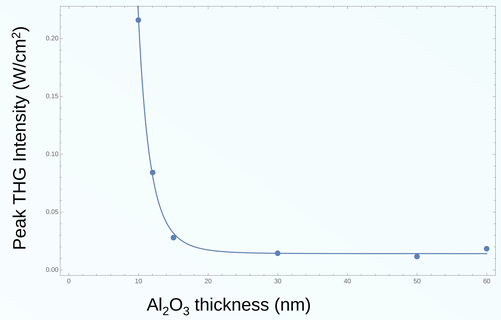
- Large Au nanoparticles (d>50nm) produce modest THG increases (8x).
- Middle size Au nanoparticles—Whose LSPR satisfies the harmonic resonant condition—exhibit the most SHG & THG enhancement (20x)
- Small Au nanoparticles (<4nm) do not exhibit any THG increases (2x).
- The lack of THG enhancement with detuned or quenched Au nanoparticle plasmon resonances indicates that harmonic pairing of the CuS and Au LSPRs is the medium by which the enhancement of THG occurs between CuS and Au nanoparticles, independent of other material properties.

Interstitial Insulating Spacer

- Examine dependence of THG enhancement on separation of Au & CuS nanoparticles
- Adding Al_2O_3 layers of controlled thicknesses to probe 10-100 nm range



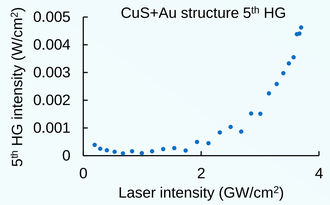
Separation Distance(nm)	Peak THG Intensity (W/cm²)
10	0.216
12	0.084
15	0.028
30	0.014
50	0.012
60	0.018

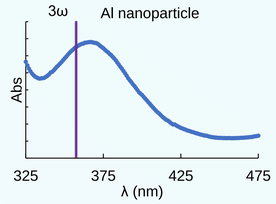


Data Fit: $0.014189 + \frac{202610}{t^6}$

Developing Directions

- Aluminum nanoparticles feature LSPR @ 3ω, could potentially be used to stimulate enhancement of higher harmonic generation.
- Tri-layer structures of CuS, Au, and Al nanoparticles with multiply harmonic resonances





Acknowledgements

The research was supported by Vanderbilt's Office of the Provost Interdisciplinary Discovery Grant. Nathan Spear supported by VINSE Graduate Fellowship. Special thanks to Dr. James Mcbride for assistance with imaging in the SEM.

References:

1) Motl, N. E.; Ewusi-annan, E.; Sines, I. T.; Jensen, L.; Schaak, R. E. Experimental Determination of Composition and Correlation with Theory. J. Phys. Chem. C 2010, 19263–19269
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