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Understanding and controlling high harmonic generation processes in hybrid materials at the nanoscale

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14. ABSTRACT
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(8 published and 2 recently submitted and under review) in leading peer-reviewed journals, 16 invited talks. Development of multiscale simulators with quantitative capabilities significantly improve our ability to efficiently design new chemical and biological sensors and characterize

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Understanding and controlling high harmonic generation processes in hybrid materials at the nanoscale

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Arizona State University

Summary

The research efforts sponsored by AFOSR NLO program led to multiple collaborative manuscripts published together with experimental and theoretical groups including AFRL lead scientist Dr. Ruth Pachter. The major goal was to develop and field-test the semi-classical hydrodynamic model of conduction electrons in metal to achieve quantitative agreement with experiments. Based on our model we were able to: (a) explain experiments on second harmonic generation by plasmonic nanocrescents; (b) guide experiments on second harmonic generation by tungsten diselenide strongly coupled to gold nanowires; (c) achieve nearly perfect agreement with experiments on second order hyperpolarizabilities of triangular nanoprisms. Our theoretical paper was chosen as the Editor Choice in 2020. Models for quantum materials combined with nonlinear optical response of plasmonic systems were developed and deployed for the first time. Our group now is the only group in the world that can simulate (both qualitatively and quantitatively) nonlinear optical phenomena at exciton-plasmon nano-interfaces. Finally, we developed a new parallel methodology that significantly reduces execution times on supercomputers and can handle both nonlinear metal response and hundreds of thousands of molecules with ro-vibrational degrees of freedom fully accounted for. Overall, the research program has led to 10 publications (8 published and 2 recently submitted and under review) in leading peer-reviewed journals, 16 invited talks. Development of multiscale simulators with quantitative capabilities significantly improve our ability to efficiently design new chemical and biological sensors and characterize nano-materials. New methodologies in nonlinear optics of exciton-plasmon systems can be used as design tools for broadband optical devices, nonlinear frequency converters, mid-infrared photonics, and THz sources and detectors.

Accomplishments

Following the original research plan, we have developed an efficient model based on the nonlinear semi-classical hydrodynamics approach. This model has been fully deployed and integrated into our home-build codes. We performed extensive numerical tests of the upgraded codes. The codes have been tuned to ensure the best scalability for DOD clusters. Below I list major research highlights resulted from this grant. At the end of this section, I list major milestones achieved.

Our manuscript published in *Journal of Physical Chemistry C* (reference #8) was a continuation of the long-term collaboration efforts with Dr. Ruth Pachter. This work went beyond a simple perturbative model of the second harmonic generation (SHG) for transition metal dichalcogenide (TMD) materials combining their nonlinear response with the one from metal nanostructures. Rigorous electrodynamical simulations based on the nonlinear Drude model were performed to investigate the influence of strong coupling on high harmonic generation by periodic metal gratings. It was shown that a thin dispersive material with a third order nonlinearity strongly coupled to surface plasmon-polaritons significantly affects even harmonics generated solely by the metal. The physical nature of this effect was explained using a simple analytical model and further supported by numerical simulations. Furthermore, the behavior of the second and third harmonics was investigated as a function of various physical parameters of the model material system, revealing highly complex dynamics. The nonlinear optical response of two-dimensional few-layer WS_2 with both second and third order susceptibilities coupled to a periodic plasmonic grating was shown to have a significant effect on the second harmonic generation of the metal.

Another important work was done in collaboration with University of Bordeaux and CRPP CNRS lab (reference #7). We applied our model to investigate optical properties of interacting dye molecules near a metal mirror. Our theoretical prediction was confirmed in brilliant experiments performed by Dr. Renaud Vallee and his colleagues. The physics of collective optical response of molecular assemblies, pioneered by Dicke in 1954, has long been at the center of theoretical and experimental scrutiny. The influence of the environment on such phenomena is also of great interest due to various important applications in e.g., energy conversion devices. In this manuscript we demonstrated both experimentally and theoretically the spatial modulations of the collective decay rates of molecules placed in proximity to a metal interface. We showed in a very simple framework how the cooperative optical response can be analyzed in terms of intermolecular correlations causing interference between the response of different molecules and the polarization induced on a nearby metallic boundary and predict similar collective interference phenomena in excitation energy transfer between molecular aggregates.

We are very proud of the manuscript (reference #6) published in *Journal of Chemical Physics*. This work was chosen as the Editor's Pick praising both physics and numerics. I was told by several colleagues that this work will become a benchmark in the field of nonlinear plasmonics. Optical properties of periodic arrays of nanoholes of a triangular shape with experimentally realizable parameters were examined in both linear and nonlinear regimes. By utilizing a fully vectorial three-dimensional approach based on the nonlinear hydrodynamic Drude model describing metal coupled to Maxwell's equations and Bloch equations for molecular emitters, we analyzed linear transmission, reflection, and nonlinear power spectra. Rigorous numerical calculations demonstrating second and third harmonic generation by the triangular hole arrays were performed. It was shown that both the Coulomb interaction of conduction electrons and the convective term contribute on equal footing to the nonlinear response of metal. It was demonstrated that the energy conversion efficiency in the second harmonic process is the highest when the system is pumped at the localized surface plasmon resonance. When quantum emitters were placed on a surface of the nano-holes' array, the second harmonic signal exhibited three peaks corresponding to second harmonics of the localized surface plasmon mode and upper and lower polaritonic states. I would like to emphasize that this manuscript is the first work, in which three models were used on equal footing, namely Maxwell's equations, semi-classical hydrodynamic model for conduction electrons, and Bloch equations to account for quantum dynamics of thousands of emitters.

The first field-test of our newly developed hydrodynamic model was to apply it to experiments. This work was done in collaboration with the experimental group at UC Irvine on nonlinear response of arrays of nanocrescents (reference #5). Experimental data show interesting asymmetry observed in SHG detected as a function of the incident polarization. Simple models could not account for such an asymmetry and stopped short of explaining where the asymmetry may come from. We utilized our fully vectorial hydrodynamics model and demonstrated that even small deviations in particles' shapes from their ideal forms (up to a few nm!) lead exactly to what experimentalists have seen. In the developing field of nonlinear plasmonics, it is important to understand the fundamental relationship between properties of the localized surface plasmon resonance (LSPR) of metallic nanostructures and their nonlinear optical responses. A detailed understanding of nonlinear responses from nanostructures with well-characterized LSPRs is an essential prerequisite for the future design of sophisticated plasmonic systems with advanced functions to control light. In this article, we investigate the second-order harmonic (SH) responses from gold nanocrescent (Au NC) antennas which have wavelength and polarization sensitive LSPRs in the visible and near-infrared wavelength ranges. The wavelength dependence of the SH intensity exhibits spectral profiles different from dipole LSPR bands in absorbance spectra. The incident polarization angle dependence was found to vary significantly when the excitation wavelength was tuned over the dipole band. Finite-difference time-domain calculations coupled with a nonlinear hydrodynamic model were carried out for Au NC arrays to investigate the local field enhancement of the incoming fundamental and emitting SH light. The experimental and theoretical results indicate that the effects of higher-order LSPRs, such as quadrupole and multipole resonances, occurring at SH wavelengths are important in governing the SH generation process. Also, it is shown that the incident polarization angle dependence of SH signals is very strongly sensitive to nanoscale variations in the NC's shape.

The next experimental challenge was to apply the full machinery of the Maxwell-hydrodynamic-Bloch equations theoretically introduced in reference #6 discussed above. Our close collaboration with experimental group from Emory University led by Prof. Hayk Harutyunyan followed our theoretical predictions of the Rabi splitting in SHG signal that one would observe in the strong coupling regime between plasmonic systems and quantum emitters. In this work (reference #4) we used the hydrodynamics model to study SHG from strongly coupled systems comprised of Au nanorods placed on WSe_2 atomically thin monolayer. We predicted that the second harmonic peak should split in two peaks in the strong coupling regime, representing second harmonics from exciton-plasmon states (that have a mixed character of both an exciton and a plasmon). This is achieved when the longitudinal plasmon frequency for a nanorod matches that of the exciton in WSe_2 and the coupling strength surpasses all damping rates. Experimental data were shown to observe this very effect! Monolayer transition metal dichalcogenides, coupled to metal plasmonic nanocavities, have recently emerged as new platforms for strong light-matter interactions. These systems are expected to have nonlinear optical properties that will enable them to be used as entangled photon sources, compact wave-mixing devices, and other elements for classical and quantum photonic technologies. We reported the first experimental investigation of the nonlinear properties of these strongly coupled systems, by observing second harmonic generation from a WSe_2 monolayer strongly coupled to a single gold nanorod. The pump frequency dependence of the second harmonic signal displays a pronounced splitting that can be explained by a coupled oscillator model with second-order nonlinearities. Rigorous numerical simulations utilizing a nonperturbative nonlinear hydrodynamic model of conduction electrons support this interpretation and reproduce experimental results. Our study thus lays the groundwork for understanding the nonlinear properties of strongly coupled nanoscale systems.

In the subsequent work (reference #3) in collaboration with Dr. Andrei Piryatinski (Los Alamos National Lab) we followed my original idea of utilizing a gain medium to enhance SHG efficiency generated at plasmonic interfaces. Using incoherently pumped quantum emitters in a close proximity of a plasmonic system (we considered a periodic array of nanopillars as an example) we investigated the behavior of the SHG efficiency. Anticipated enhancement may happen since metal induces coherences in emitters, which in turn may enhance the local electric field at the fundamental frequency thus significantly increasing SHG efficiency. We generalized the driven-dissipative Tavis–Cummings model by introducing the anharmonic surface plasmon-polariton mode coupled to emitters and examine physical properties of corresponding polariton states. Our calculations of the SHG efficiency for strong coupling indeed demonstrated orders of magnitude enhancement facilitated by the polariton gain. We further discussed time-domain numerical simulations of SHG in a square lattice comprising Ag nanopillars coupled to emitters utilizing a fully vectorial nonperturbative nonlinear hydrodynamic model for conduction electrons coupled to Maxwell–Bloch equations for emitters. The simulations supported the idea of gain enhanced SHG and show orders of magnitude increase in the SHG efficiency as the emitters were tuned in resonance with the lattice plasmon mode and brought above the population inversion threshold by incoherent pumping. By varying pump frequency and tuning emitters to an LSPR mode, we demonstrated further enhancement of the SHG efficiency facilitated by strong local electric fields.

One of the fundamental questions we could address using our numerical model was to investigate whether polariton states formed in the strong coupling regime between quantum emitters and a plasmonic system participate in the nonlinear dynamics. To tackle this question (reference #2) we scrutinized SHG from hexagonal periodic arrays of triangular nano-holes of Al using a self-consistent methodology based on the hydrodynamics-Maxwell–Bloch approach. It was shown that angular polarization patterns of the far-field second harmonic response abide to three-fold symmetry constraints on tensors. When a molecular layer was added to the system and its parameters were adjusted to achieve the strong coupling regime between a localized plasmon mode and molecular excitons, Rabi splitting was observed from the occurrence of both single- and two-photon transition peaks within the SHG power spectrum. We argued that the splitting observed for both transitions resulted from *direct two-photon transitions between lower and upper polaritonic states of the strongly coupled system*. This interpretation could be accounted by a tailored three-level quantum model, with results in agreement with the unbiased numerical approach. Our results suggested that the hybrid states formed in strongly coupled systems directly contribute to the nonlinear dynamics. This opens new directions in designing THz sources and nonlinear frequency converters. I note that the direct observation of two-photon transitions between polariton states was possible only because of the model we developed.

At the end of the grant, I was approached by experimental group from France (led by Prof. Isabelle Ledoux-Rak known for her amazing experiments in colloidal chemistry and nonlinear optics) asking to apply our Maxwell-hydrodynamic model to calculate a second order hyperpolarizability of triangular nano-prisms. The question was to perform systematic studies of such particles examining SHG vs. sharpness of particle's corners. In her experiments Prof. Ledoux-Rak managed to extract hypolarizabilities from SHG spectra for various surface-to-volume ratios and different curvatures. We developed the numerical procedure that allows extracting hyperpolarizabilities of an arbitrary order using our Maxwell-hydrodynamic model. Moreover, we could directly compare our results with experiments on a quantitative level. The comparison was remarkably good! Experimental value of the hyperpolarizability for a given nano-prism (with dimensions extracted from TEM images) was reported at 1.30×10^{-33} SI units while our simulations (using experimental dimensions) led to the value of 1.43×10^{-33} SI units thus proving that the developed model not only can be used as a qualitative tool but also has quantitative predictive power. The results of this work were recently submitted and are currently under review.

We have developed and deployed a multiscale numerical code that simulates electrodynamics in time domain for exciton-plasmon systems with molecules taking their ro-vibrational degrees of freedom explicitly into account. The code combines Maxwell's equations, semi-classical hydrodynamics model for conduction electrons in metal, and the Schrödinger equation for molecules with numerical propagation of ro-vibrational wavepackets on user-defined electronic potential energy surfaces. Such code implements double layer parallel strategy i.e., three-dimensional domain decomposition technique for Maxwell's and hydrodynamics equations and equal redistribution of the quantum dynamics on all processors. The code can handle thousands of molecules and its execution time scales nearly linearly with a number of processors allowing us to simulate systems on a large scale.

Impacts

The methodology developed under this grant opens several exciting research directions in nonlinear nano-optics. We were the first group to combine nonlinear electrodynamics with quantum dynamics at nanoscale interfaces, which led to several predictions later experimentally confirmed. Moreover, our deployed codes have quantitative power as we recently demonstrated when comparing simulations with experimental data. Development of multiscale simulators with quantitative capabilities significantly improve our ability to efficiently design new chemical and biological sensors and characterize nano-materials. New methodologies in nonlinear optics of exciton-plasmon systems can be used as design tools for broadband optical devices, nonlinear frequency converters, mid-infrared photonics, and THz sources and detectors.

List of Publications, Presentations, and Invited Lectures resulted from the grant

SUBMITTED PAPERS UNDER REVIEW

1. "High yield synthesis and quadratic nonlinearities of gold nanoprisms in solution: the role of corner sharpness", H. M. Ngo, E. Drobnyh, M. Sukharev, T. T. Luong. J. Zyss. I. Ledoux-Rak, *Israel Journal of Chemistry* (submitted, 2022).
2. "Coupling, lifetimes, and "strong coupling" maps for single molecules at plasmonic interfaces", M. Mondal, M. A. Ochoa, M. Sukharev, A. Nitzan, *Journal of Chemical Physics* (submitted, 2021).

PUBLISHED AND ACCEPTED PAPERS IN THE REFEREED JOURNALS

1. "Strong coupling between an inverse bowtie nano-antenna and a J-aggregate", A. Weissman, M. Sukharev, A. Salomon, *Journal of Colloid and Interface Science* **610**, 438 (2021).
2. "Second harmonic generation by strongly coupled exciton-plasmons: the role of polaritonic states in nonlinear dynamics", M. Sukharev, A. Salomon, J. Zyss, *Journal of Chemical Physics* **154**, 244701 (2021).
3. **"**Second-harmonic generation in nonlinear plasmonic lattices enhanced by quantum emitter gain medium", M. Sukharev, O. Roslyak, A. Piryatinski, *Journal of Chemical Physics* **154**, 084703 (2021).

4. "Second harmonic generation from a single plasmonic nanorod strongly coupled to a WSe_2 monolayer", C. Li, X. Lu, A. Srivastava, S. D. Storm, R. Gelfand, M. Pelton, M. Sukharev, H. Harutyunyan, *Nano Letters* **21**, 1599 (2020).
5. "Wavelength and polarization dependence of second harmonic responses from gold nanocrescent arrays", H. Maekawa, E. Drobnyh, C. A. Lancaster, N. Large, G. C. Schatz, J. S. Shumaker-Parry, M. Sukharev, N.-H. Ge, *Journal of Physical Chemistry C* **124**, 20424 (2020).
6. "Plasmon enhanced second harmonic generation by periodic arrays of triangular nanoholes coupled to molecular emitters", E. Drobnyh and M. Sukharev, (Editor's Choice) *Journal of Chemical Physics* **152**, 094706 (2020).
7. "Energy transfer and interference by collective electromagnetic coupling", M. Gómez-Castaño, A. R. Cubero, L. Buisson, J. L. Pau, A. Mihi, S. Ravaine, R. A. L. Vallée, A. Nitzan, M. Sukharev, *Nano Letters* **19**, 5790 (2019).
8. "Harmonic generation by metal nanostructures optically coupled to a few-layer thin transition metal dichalcogenides", E. Drobnyh, R. Pachter, M. Sukharev, *Journal of Physical Chemistry C* **123**, 6898 (2019).

Presentations and seminars

1. Invited webinar, *Nonlinear optics at exciton-plasmon interfaces*, Polariton Chemistry Webinar, April 14, 2021.

2. Journal of Chemical Physics Editor's Choice Awards "*Plasmon enhanced second harmonic generation by periodic arrays of triangular nanoholes coupled to molecular emitters*", APS March meeting, March 16, 2021.

3. Invited physics webinar, Center for Photonics and Quantum Materials, Skolkovo Institute of Science and Technology, Moscow, Russia, November 25, 2020.

4. Invited physics webinar, Pabna University of Science and Technology, Bangladesh, October 28, 2020.

5. Western Kentucky University, Physics webinar, October 4, 2020

6. Metamaterials 2020, virtual conference, September 28 – October 3, 2020.

7. *"Predicting and understanding optical properties of exciton-plasmon nanomaterials"*, invited talk, Chemical Physics Seminar, Tel Aviv University, December 19, 2019.

8. *"Optics of exciton-plasmon materials"*, invited talk, Center for Integrated Nanotechnologies (CINT) 2019 Annual Meeting, Los Alamos National Laboratory, September 22 – 24, 2019.

9. *"Electrodynamics of exciton-plasmon materials: strong coupling and beyond"*, invited talk, Gordon Research Conference, Quantum Control of Light and Matter, Salve Regina University, August 11 – 16, 2019.

10. *"Electrodynamics of exciton-plasmon materials: strong coupling and beyond"*, invited talk, the Penn Conference on Theoretical Chemistry, August 14 – 16, 2019.

11. *"Exciton-plasmon materials go nonlinear"*, invited talk, **TSRC Conference**, Nanophotonics out of equilibrium, Telluride, Colorado, July 16 – 20, 2019.

12. *"Crafting light-matter interactions at plasmonic interfaces: strong coupling and beyond"*, invited talk, TSRC Conference, Nonequilibrium Phenomena, Nonadiabatic Dynamics and Spectroscopy, Telluride, Colorado, July 16 – 20, 2019.

13. *"Crafting light-matter interactions at plasmonic interfaces: strong coupling and beyond"*, invited seminar, Weizmann Institute of Science, June 18, 2019.

14. "*Crafting the light-matter interactions at metal interfaces: strong coupling and beyond*", invited colloquium, Nanoscience Seminar, Arizona State University, March 18, 2019.

15. "*Exciton-plasmon nanosystems: modeling, understanding, and predicting new phenomena*", invited colloquium, College of Optical Sciences, University of Arizona, November 15, 2018.

16. "*Calculating optical response of hybrid materials at the nanoscale: the need for speed*", invited talk, DOD HPC Users Meeting, Wright-Patterson Air Force Base, September 24-28, 2018.