

# Plasmon-mediated nonlinear optics and dynamics

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## INTRODUCTION

Nonlinear optical (NLO) processes provide the foundation for many important technologies, which include but are not limited to optical communication and computing,<sup>1</sup> laser technology,<sup>2</sup> optical limiting materials,<sup>3</sup> molecular spectroscopy,<sup>4</sup> imaging,<sup>5,6</sup> and sensing.<sup>7</sup> Hence, methodologies that increase NLO efficiency can have considerable benefits for fundamental research and large societal impacts.

The state-of-the-art in second harmonic generation is achieved using multiple quantum wells, which transduce fundamental light to harmonic frequencies with second-order susceptibilities exceeding  $10^3$  pm/V.<sup>8,9</sup> These record-breaking values are reached by resonance matching of both the fundamental and harmonic electromagnetic frequencies with the intersubband energy offsets of the material. However, these systems are generally limited to functioning in the far-infrared because of their small intersubband energy differences. Plasmons have the potential to transform nonlinear optics because the resonance frequencies of these systems can be synthetically tuned across a large range of the electromagnetic spectrum all the way to the ultraviolet.<sup>10,11</sup> Indeed, plasmon resonances have already been used to transduce perturbative second and third harmonic generation,<sup>12,13</sup> multi-photon photoluminescence,<sup>14</sup> and four-wave mixing.<sup>15</sup> In addition to changing frequency, plasmonic nanoparticles have been used to modulate the polarization state of light transduced in NLO processes.<sup>16</sup> These modulations have been accomplished using the geometric structure of nanoparticle assemblies and the lattice structure of isolated nanoparticles.<sup>17,18</sup> However,

progress in a few key areas is still needed to realize the full potential of plasmon-mediated nonlinear optics. In particular, strategies that can minimize energy loss and improve resonance matching are essential. Critical components of these efforts will include designing hybrid nanostructures that increase plasmon-mode quality factors and understanding electronic relaxation dynamics that compete with desired NLO pathways. Still, other strategies that allow time-delayed amplification of NLO signals can be advantageous for molecular spectroscopy and sensing. Advances in some of these areas are described in this Special Topic issue.

## SUMMARY OF AREAS COVERED

Several papers in this Special Topic issue highlight the strategic assembly of plasmonic nanoparticles to increase NLO signal strengths that span a large wavelength range. One manuscript provides a comprehensive study of nonlinear optical responses in plasmonic nanoparticles with  $C_{2v}$  symmetry, specifically focusing on L-shaped, nanocrescent, and split-ring resonator configurations.<sup>19</sup> Using computational models, the authors explore SHG and terahertz (THz) generation under both continuous wave (CW) and pulsed excitations and determine that each shape's unique geometry and symmetry play crucial roles in determining SHG polarization states and selection rules. In addition, for pulsed excitations, THz emission spectra exhibit notable geometry-dependent features, suggesting potential applications in THz sensing and nonlinear spectroscopy. The theoretical survey provides a roadmap for future

experimental research to realize tailored, structure-dependent NLO responses. A related experimental paper demonstrates the use of plasmonic “dolmen” trimer systems for mediating high-order multi-photon photoluminescence.<sup>20</sup> This manuscript demonstrates that hybrid mode-selective excitation in dolmen structures, incorporating high-angular momentum dark modes, can control multi-photon absorption due to precise tuning of plasmon behavior at sub-femtosecond timescales. In a related paper on plasmonic nanobowls, dark-field excitation of dark modes is reported to yield persistent plasmon coherences extending to 12 fs.<sup>21</sup> The extended lifetimes obtained for both the dolmen and nanobowl nanostructures serve to improve material quantum yields and increase NLO responses. Another study investigates plasmon-mediated nonlinear dynamics and lasing properties of nanoemitters embedded within a lattice of nanorings. From this, the authors determine a critical plasma frequency for achieving controllable lasing in photonic devices and highlight emerging trends in tunable plasmonic systems.<sup>22</sup>

A related computational study examines second- and third-harmonic generation in gold nanorod assemblies through the use of a real-time time-dependent density functional tight binding (RT-TDDFTB) approach.<sup>23</sup> By modeling nonlinear signals from time-dependent dipole responses under various laser pulse parameters, the study shows how intensity, duration, frequency, and polarization impact harmonic generation efficiency in single and dimer nanorod systems. The findings show that SHG occurs for end-to-end arrangements that cause symmetry-breaking, while THG is generated from both single and dimer structures. The research also explores how variations in nanorod length affect plasmon energies and harmonic response, providing polarizability and hyper-polarizability estimates, which is a valuable and much-needed resource for predictive plasmon-mediated nonlinear optics. A related computational study that evaluates time-dependent Raman signals provides new insights into how to simulate incident electromagnetic field profiles, which is essential for accurate modeling of experimental measurements and photonic device applications.<sup>24</sup>

Another theme covered in this Special Topic is the use of hybrid nanostructures for increasing signal strength and controlling dynamics. One computational study shows that the optical and electronic interactions between a molecule and a nanocavity can substantially influence plasmon behavior.<sup>25</sup> In particular, the specific orientation of molecules in the nanocavity gap, along with gap morphology, modifies the molecular energy levels with respect to the Fermi level of the metal, which in turn controls charge-transfer resonance intensities. Plasmon–exciton charge-transfer interactions are also shown experimentally in multi-component systems.<sup>26</sup> This study investigates ultrafast charge carrier dynamics in CsPbBr<sub>3</sub> perovskite quantum dots (PQDs) coupled with gold nanoparticles. Using ultrafast spectroscopy, the authors resolve efficient electron transfer from PQDs to AuNPs, which competes favorably with charge carrier trapping at shallow and deep trap states, thereby minimizing detrimental energy losses. This dynamic behavior offers insights into the design of hybrid nanostructures for enhanced energy transfer and nonlinear optical processes. These hybrid systems underscore the potential for plasmon–exciton interactions in nonlinear and quantum optics.

Multiple papers describe the use of plasmonic nanoparticles for driving high-order nonlinear processes. High harmonic generation by aluminum and sodium nanoparticles is predicted as a strategy to

achieve high flux extreme ultraviolet laser pulses.<sup>27</sup> In this study, the so-called “poor” metals are suggested to have advantages over noble metals because of minimized dephasing by interband excitations. A related theoretical study explores the near-field excitation dynamics of a sodium atom chain (Na<sub>10</sub>) and a Na<sub>10</sub>–N<sub>2</sub> complex.<sup>28</sup> By locally exciting Na<sub>10</sub> with a near-field optical pulse under on- and off-resonant conditions, the study reveals that resonant excitation produces delocalized states throughout the chain, while off-resonant excitation results in localized responses. When coupled with an N<sub>2</sub> molecule, the Na<sub>10</sub> chain acts as an energy-transfer conduit, with energy propagation dependent on the orientation of N<sub>2</sub> relative to the chain. These findings suggest many exciting potential applications in remote excitation at atomic scales, which could be useful for the design of photonic and optoelectronic devices at the nanoscale.

Continuing with the theme of non-traditional and hybrid plasmonic materials, several authors explore plasmon-mediated synthesis of new systems that could be impactful for nonlinear optics. One paper explores the plasmon-induced site-selective growth of silver onto gold nanocubes, forming Au–Ag heteronanostructures with unique anisotropic shapes.<sup>29</sup> By selectively exciting two different localized surface plasmon resonance (LSPR) modes in the AuNCs, the authors achieve distinct morphologies: distal mode excitation results in Ag growth on the top of the AuNCs, while proximal–distal mode excitation causes lateral Ag growth. This exciting result shows the promise of using plasmon-mode selective excitation for developing new polarized NLO transducers. A related paper describes the growth dynamics of silver–gold core–shell nanoparticles.<sup>30</sup> Another study explores the transformation of pyrolytic carbon into luminescent, graphitized carbon dots (CDs) on silver gratings through the activation of surface plasmons.<sup>31</sup> The realization of new plasmonic materials, such as these, is likely to open new opportunities for photonic and nonlinear optics research and applications.

## CONCLUSIONS

In summary, this Special Topic issue presents many exciting advancements of plasmon-mediated nonlinear optics and dynamics, which will have a significant impact on chemical research, molecular sensing, laser pulse technology, and many other photonics applications. These advances offer fresh insights into near-field light–matter interactions and provide new opportunities for technological developments, especially at the intersections of materials science, photonics technology, and applied spectroscopy. This Special Topic issue reflects the extremely high level of activity in these research areas and the breadth of research methods being brought to the fore for new discovery. As such, prospects for future research breakthroughs and overcoming the challenges identified in the opening paragraphs are high. Moreover, this Special Topic highlights studies of the interaction between plasmonic nanoparticles and light at frequencies spanning the extreme ultraviolet to terahertz range. This is a frontier of plasmonics research that can open new opportunities for photonic integrated circuits and molecular and biological sensing, especially through the use of remote excitation. Finally, hybrid plasmonic nanostructures could be used to create new optical transitions, leading to new lasers and advancements in areas such as quantum computing, quantum communication, and quantum sensing. Plasmon-mediated nonlinear optics is also poised to establish

new research directions with implications to the field of chemical physics.

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### Author Contributions

**Kenneth L. Knappenberger, Jr.:** Conceptualization (equal); Writing – original draft (equal); Writing – review & editing (equal). **Emiko Kazuma:** Writing – review & editing (equal). **Olivier J. F. Martin:** Writing – review & editing (equal). **Matthew T. Sheldon:** Writing – review & editing (equal).

## DATA AVAILABILITY

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

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