Editorial

Plasmon-exciton coupling

https://doi.org/10.1515/nanoph-2019-0065

This journal describes its scope as focusing on "the interaction of photons with nano-structures", a definition of nanophotonics that we believe most researchers in the field would agree with. Fundamental research in nanophotonics thus primarily involves understanding optically-induced excitations in nano-scale materials and how the properties of these excitations depend on the size, shape, and arrangement of the nano-structures. Two classes of excitation, in particular, have inspired extensive research: plasmons in metal nano-structures, and excitons in molecular or semiconductor materials. Plasmons are collective oscillations of conduction electrons in metals, and coupling of light to plasmon resonances in metal nano-structures has attracted attention primarily because of their ability to concentrate optical fields to volumes well below the diffraction limit [1]. Excitons are bound electron-hole pairs in molecules or semiconductors, and excitons in semiconductor nanocrystals, or quantum dots, have attracted particular attention because of their size-dependent transition frequencies and efficient optical emission [2].

New phenomena can arise when plasmons and excitons in nano-structures are coupled to one another. As for many current topics in nanophotonics, the origins of research into plasmon-exciton coupling can be traced to the 1970s and early 1980s, when it was first demonstrated that metal films and metal particles could enhance optical absorption and emission in adjacent dye molecules [3, 4]. Studies of plasmon-exciton coupling accelerated during the general revival of plasmonics in the late 1990s, as improved fabrication and characterization techniques enabled systematic study and optimization of coupled metal-molecule and metal-semiconductor structures. Through extensive theoretical and experimental studies, a comprehensive understanding of plasmon-enhanced absorption and emission has emerged [5, 6]. Because several scientific communities have been involved in developing this understanding, different descriptions have arisen for the same underlying phenomena. Electrical engineers, for example, tend to describe a plasmonic metal nano-structure as an optical antenna that receives optical energy from the far field and uses it to excite an exciton, or that transmit optical energy from an exciton to the far field [7, 8]. Chemists, by contrast, often describe plasmon-enhanced emission in terms of energy transfer from an exciton to a plasmon and the subsequent radiative or non-radiative decay of the plasmon [9, 10].

A description popular among physicists connects plasmon-modified emission to the modification of spontaneous-emission rates for atoms, molecules, and other emitters in optical cavities, a field known as cavity quantum electrodynamics (cavity QED) [11]. In this description, modified emission rates correspond to the weak-coupling regime of cavity QED, where the cavity or plasmonic nanostructure serves to modify the available electromagnetic density of states for spontaneous emission. The description immediately raises the possibility of achieving with plasmonic systems the strong-coupling regime of cavity QED [12], where spontaneous emission is no longer irreversible, but energy is coherently exchanged between the emitter and the plasmon, forming new hybrid states known as polaritons (or sometimes as plexcitons). As strong coupling between single atoms and cavities has long been investigated as an enabling technology for quantum-information platforms [13], strong coupling between single excitons and plasmons has the promise of enabling similar applications in nanophotonic systems with the potential for integrability and room-temperature operation.

The promise and excitement of the field inspired a group of scientists to assemble, in June 2018, at the Telluride Science Research Center in Telluride, CO, USA for a workshop on Plasmon-Exciton Coupling. During presentations and discussions at the workshop, four interrelated research directions emerged: (1) the development of methods for fabricating systems with strong and controlled plasmon-exciton interactions; (2) the use of new excitonic material systems; (3) plasmonic enhancement of excitonic processes beyond absorption and luminescence; and (4) room-temperature strong, very strong, and ultra-strong plasmon-exciton coupling. This Special Issue collects review papers and reports of original research in each of these directions, illustrating the state-of-the-art of the field.

Underlying any attempt to observe new phenomena in plasmon-exciton coupling or to exploit the phenomena for new applications is the need to fabricate nanoscale systems with plasmonic and excitonic components whose size, shape, number, and arrangement are controlled. Szychowski et al. [14] review strategies that have been employed to

couple plasmonic metal nanoparticles with semiconductor nanocrystals, or quantum dots (QDs), focusing on QDs as model excitonic systems because of their large oscillator strengths, tunable transition frequencies, and photostability. They emphasize techniques that use chemical functionalization and self-assembly, because of their unique capability to provide sub-nanometer control over interparticle spacing. They also point out a primary challenge of this method: the difficulty in obtaining a uniform sample of assemblies with precise control over the number and arrangement of the coupled particles. Many et al. [15] show an example of how this challenge may be overcome, demonstrating the synthesis of assemblies composed of 12 gold patches regularly arranged at the centers of the faces of a dodecahedron. Notably, the assemblies are produced in solution at the gram scale and with high uniformity. They demonstrate the utility of such uniform assembly techniques by demonstrating an unprecedented bulk magnetic response at optical frequencies, which arises due to interactions among the gold patches in the assemblies. The application of similar control to heterogeneous assemblies has the promise to enable strong and controlled plasmon-exciton interactions.

Another means to optimize plasmon-exciton interactions is to employ novel excitonic materials. The use of QDs already represents an improvement over the molecular systems that were the focus of early investigations. Bitton et al. [16] review the physics of plasmon-QD coupling and experimental results in the field. They emphasize a clear trend of increasing plasmon-exciton coupling strength over the years, culminating in the current status of room-temperature strong coupling between single excitons and single plasmons, and pointing towards potential applications in quantum information. Cortufo et al. [17] review the use of two-dimensional transition metal dichalcogenides (TMDs) as excitonic materials for coupling to plasmons. As well as supporting excitons with large oscillator strengths at room temperature, TMDs can support localized excitons that act as single-photon emitters, and they are readily integrated with fabricated metal nanostructures at single-nanometer-scale distances. Moreover, they present a unique opportunity to exploit the valley degree of freedom: TMDs support two non-equivalent pairs of band extrema at opposite ends of the Brillouin zone, with carriers in the different valleys having opposite spins. These two valleys can be separately addressed optically by using the circular polarization of light, and thus enable new modes of plasmon-exciton interaction without analog in other materials.

This is an example of a new mode of plasmon-exciton interaction, a theme that is picked up by several authors, including Roman and Sheldon [18]. These authors also take advantage of a new material class – namely, cesium lead halide perovskite nanocrystals – that demonstrates a host of unusual optical properties. In particular, the nanocrystals exhibit an unusually high efficiency for one-photon up-conversion, or anti-Stokes photoluminescence (ASPL), in which an incident photon is absorbed, the excited electron is promoted to a higher-energy state by a lattice vibration, and then a higher-energy photon is emitted. This process involves the removal of thermal energy from the material and can be used for optical cooling if the efficiency is high enough. The authors show that coupling perovskite nanocrystals to plasmonic nanostructures leads to an overall increase by a factor of 6 in the rate at which thermal energy is extracted from the system. Mousavi et al. [19] investigate the process of coherent frequency conversion in engineered plasmonic nanostructures, focusing on second-harmonic generation (SHG) as an illustrative example. Although efficient local SHG has long been observed in plasmonic systems, a quantitative understanding of the process and how it relates to the nanostructure geometry is still lacking. The authors point out the importance of phase matching for SHG in arrays of metal nanostructures. This has previously been neglected because of the assumption that phase matching would be unimportant when the interaction length in which frequency conversion takes place is small compared to the optical wavelength. The insight into the continued relevance of phase matching will help guide the development of coupled plasmon-exciton systems with ultrastrong resonant optical nonlinear response. Kholmicheva et al. [20] review the process of plasmon-induced resonance energy transfer (PIRET), in which a plasmon is optically excited and then transfers its energy by dipole-dipole coupling to an adjacent excitonic material. The effect is to greatly increase the amount of optical energy that is converted into excitons, compared to what would be absorbed by the excitonic material in the absence of the plasmonic nanostructures. The mechanism thus has the potential to increase the efficiency of thin-film solar cells or photocatalysis. Khurgin [21] considers new phenomena that can arise when coupling plasmons to excitons in bulk semiconductors or epitaxial quantum wells. These materials support delocalized Wannier-Mott excitons with Bohr radii of many lattice constants, as compared to the small-radius Frenkel excitons in molecular materials or the highly confined excitons in QDs and TMDs. Considering the specific system of excitons in CdS coupled to Ag nanoparticles, the author predicts a reduction of the excitonic radius by a factor of 3 in the plasmon-exciton polaritons, binding of the polaritons to a shell within a few nanometers of the Ag nanoparticle, and stability of the polaritons at

room temperature. Together, these raise the possibility of novel physical phenomena, such as the room-temperature dynamical condensation of polaritons.

The phenomena predicted in [21] occur when the plasmon-exciton coupling strength exceeds the exciton binding energy. The author calls this "very strong coupling", to distinguish it from the strong-coupling regime, where the coupling strength exceeds decoherence rates in the system, and the ultrastrong-coupling regime, where the coupling strength is a significant fraction of the exciton transition frequency. These regimes, as well as the broader parameter space of polaritonics, are reviewed by Ballarini and de Liberato [22]. As well as the coupling strength, another key parameter is the number of excitons, N, involved in coupling to a plasmonic resonance. Strong nonlinearities arise as $N \rightarrow 1$, whereas collective phenomena such as polaritonic condensation become possible for large N. The authors emphasize how the parameter space can be accessed through the design of the polaritonic systems, particularly the transition between photonic and plasmonic cavities. They also discuss the role of the excitonic material in this parameter space, connecting to [21] by discussing the different properties of Frenkel and Wannier-Mott excitons, and connecting to [17] by discussing how TMDs can exhibit properties associated with both classes of excitons.

As well as exemplifying the state-of-the-art, this collection of papers points towards future directions in the study of plasmon-exciton coupling. The majority of work in the field can be seen as taking the phenomena that have been demonstrated in cavity QED and moving them down to the nanoscale by using sub-diffraction-limited plasmonic nanocavities. This small mode volumes of these nanocavities have enabled a major quantitative increase in coupling strength. The next step, suggested by many of the papers in this collection, may be to go beyond these quantitative advances in order to demonstrate and exploit phenomena that are qualitatively different than those that can be achieved through coupling to conventional optical cavities. For example, plasmonic nanostructures have the unique capability of enabling ultrastrong coupling, and the nonlinear-optical phenomena that this non-perturbative regime would enable remain relatively unexplored. Pushing even further, one can expect a new regime of nonlinear and quantum optics if ultrastrong coupling can be achieved at the single-exciton level. In another direction, the bottom-up assembly techniques that have been used to form hybrid plasmon-exciton assemblies raise the possibility of achieving strong coupling and other novel optical properties in macroscopic ensembles, rather than individual microfabricated structures. The resulting bulk metamaterials are sure to enable applications that are qualitatively different from the applications enabled by single devices.

It is perhaps fitting to conclude by quoting a passage from [21], which refers specifically to Wannier-exciton plasmon polaritons, but which can be taken to refer to the entire field of plasmon-exciton coupling: "At this point it would be prudent to avoid overhyping this new phenomenon and not to dazzle the reader with an expansive array of potential transforming applications … in every walk of life, as is regrettably often done with a great detriment to science. And yet, in my view, the remarkable physics of [these systems] should be further explored in different geometries and material systems so that eventually applications, perhaps unanticipated, will materialize". We are optimistic that the continued exploration of fundamental processes in plasmon-exciton coupling will lead to applications that have not yet been imagined.

References

[1] Pelton M, Bryant G. Introduction to metal-nanoparticle plasmonics. Hoboken, NJ, John Wiley & Sons, 2013.
[2] Klimov VI, ed. Nanocrystal quantum dots, 2nd ed. Boca Raton, FL, CRC Press, 2010.
[3] Drexhage KH. IV Interaction of light with monomolecular dye layers. In: Wolf E, ed. Progress in optics. Vol. 12. Amsterdam, Netherlands, North Holland, 1974, 193–232.
[4] Glass AM, Liao PF, Bergman JG, Olson DH. Interaction of metal particles with adsorbed dye molecules: absorption and luminescence. Opt Lett 1980;5:368–70.
[5] Pelton M, Aizpurua J, Bryant G. Metal-nanoparticle plasmonics. Laser Photonics Rev 2008;2:136–59.
[6] Pelton M. Modified spontaneous emission in nanophotonic structures. Nat Photon 2015;9:427–35.
[7] Farahani JN, Pohl DW, Eisler H-J, Hecht B. Single quantum dot coupled to a scanning optical antenna: a tunable super emitter. Phys Rev Lett 2005;95:017402.
[8] Kühn S, Håkanson U, Rogobete L, Sandoghdar V. Enhancement of single-molecule fluorescence using a gold nanoparticle as an optical nanoantenna. Phys Rev Lett 2006;97:017402.
[9] Wokaun A, Lutz H-P, King AP, Wild UP, Ernst RR. Energy transfer in surface enhanced luminescence. J Chem Phys 1998;79:509–14.

[10] Dulkeith E, Morteani AC, Niedereichgolz T, et al. Fluorescence quenching of dye molecules near gold nanoparticles: radiative and nonradiative effects. Phys Rev Lett 2002;89:203002.
[11] Walther H. Experiments on cavity quantum electrodynamics. Phys Rep 1992;219:263–81.
[12] Sanchez-Mondragon JJ, Narozhny NB, Eberly JH. Theory of spontaneous-emission line shape in an ideal cavity. Phys Rev Lett 1983;51:550–3.
[13] Raimond JM, Brune M, Haroche S. Manipulating quantum entanglement with atoms and photons in a cavity. Rev Mod Phys 2001;73:565–82.
[14] Szychowski B, Pelton M, Daniel M-C. Preparation and properties of plasmonic-excitonic nanoparticle assemblies. Nanophotonics 2019;8:517–47.
[15] Many V, Dézert R, Duguet E, et al. High optical magnetism of dodecahedral plasmonic meta-atoms. Nanophotonics 2019;8:549–58.
[16] Bitton O, Gupta SN, Haran G. Quantum dot plasmonics: from weak to strong coupling. Nanophotonics 2019;8:559–75.
[17] Cotrufo M, Sun L, Choi J, Alù A, Li X. Enhancing functionalities of atomically thin semiconductors with plasmonic nanostructures. Nanophotonics 2019;8:577–98.
[18] Roman BJ, Sheldon MT. Six-fold plasmonic enhancement of thermal scavenging via $CsPbBr_3$ anti-Stokes photoluminescence. Nanophotonics 2019;8:599–605.
[19] Mousavi SHS, Lemasters R, Wang F, et al. Phase-matched nonlinear second-harmonic generation in plasmonic metasurfaces. Nanophotonics 2019;8:607–12.
[20] Kholmicheva N, Romero LR, Cassidy J, Zamkov M. Prospects and applications of plasmon-exciton interactions in the near-field regime. Nanophotonics 2019;8:613–28.
[21] Khurgin JB. Pliable polaritons: Wannier exciton-plasmon coupling in metal-semiconductor structures. Nanophotonics 2019;8:629–39.
[22] Ballarini D, De Liberato S. Polaritonics: from microcavities to sub-wavelength confinement. Nanophotonics 2019;8:641–54.

Matthew Pelton
Department of Physics, UMBC (University of Maryland, Baltimore County), 1000 Hilltop Circle, Baltimore, MD 21250, USA, e-mail: mpelton@umbc.edu

Matthew Sheldon
Department of Chemistry, Texas A&M University, PO Box 30012, College Station, TX 77843, USA, e-mail: sheldonm@tamu.edu

Jacob Khurgin
Department of Electrical and Computer Engineering, Johns Hopkins University, Barton Hall 314, Baltimore, MD 21218, USA, e-mail: jakek@jhu.edu