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Editorial

Speeding up Nanoscience and Nanotechnology with Ultrafast Plasmonics

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ABSTRACT: Surface plasmons are collective oscillations of free electrons at the interface between a conducting material and the dielectric environment. These excitations support the formation of strongly enhanced and confined electromagnetic fields. As well, they display fast dynamics lasting tens of femtoseconds and can lead to a strong nonlinear optical response at the nanoscale. Thus, they represent the perfect tool to drive and control fast optical processes, such as ultrafast optical switching, single photon emission, as well as strong coupling interactions to explore and tailor photochemical reactions. In this Virtual Issue, we gather several important papers published in *Nano Letters* in the past decade reporting studies on the ultrafast dynamics of surface plasmons.

The knowledge of both the spatial and temporal structure of an optical field interacting with a nanomaterial can enable a wider understanding of light−matter interactions at the nanoscale. In the past years, the plasmonics community have reached a broad understanding of many light-driven phenomena in their ground state. Temporal dynamics of the excited states are instead, on one side, quite challenging to explore, and, on the other side, crucial to disclose and understand novel and unexpected fundamental nanoscale physical and chemical processes. Unlike conventional optics, plasmonics enables unrivaled concentration of light well beyond the diffraction limit. Surface plasmons, the collective oscillations of free electrons at the interface between a conducting material, such as a noble metal, and the dielectric environment, support the formation of extremely confined and enhanced electromagnetic fields at the nanoscale. They display fast dynamics, on the order of tens of femtoseconds, thus making pump−probe spectroscopy one of the most widely used techniques to undertake fundamental studies on their temporal response. A pump−probe experiment typically uses a pump beam to excite the material of interest. A probe beam monitors changes that take place upon pump excitation, such as material transmission and/or absorption. By varying the time at which pump and probe beams interact with the sample, this technique allows one to study the temporal evolution of the electronic charge dynamics responsible for the changes observed in the optical response, as well as for a plethora of related nonlinear optical phenomena.

In this framework, Hanke and co-workers were one of the first teams studying the fs-dynamics of plasmonic modes supported by gold nanoantennas with different shapes. They showed that the nonlinear frequency conversion efficiency is directly linked to the plasmon radiative damping times, and that nanoantennas with the smallest volume generate by far the strongest third-harmonic signal.[1] The same year, Biagioni and colleagues investigated the temporal dynamics of both two- and four-photon photoluminescence in gold nanoantennas, demonstrating how the selection of either process can be controlled at will by choosing a suitable laser pulse duration.[2] Furthermore, Zeuner and co-workers used a coupled three-nanorod structure and phase-dependent ultrafast excitation to achieve coherent control of the nonlinear response of plasmonic modes by tuning the phase relation between two orthogonally polarized light fields via damping effects.[3] While Fourier-limited pulse duration in pump−probe experiments can allow the best temporal resolution, to improve the spatial resolution and access information on the nanometer scale, Hensen and co-workers proposed a time-resolved interferometric photoemission electron microscopy scheme, where the dynamics of the local plasmonic modes has been resolved on the fs time-scale and on a 12 nm size-scale.[4] With this approach, they were able to resolve the spatial variations of the quality factor of single plasmonic resonances, and showed, by using the theory of quasi-normal modes, that these variations are due to crosstalk between spectrally adjacent resonances. The nanometer engineering of plasmons through a proper nanostructure design is indeed fundamental to develop future plasmonic nanodevices. Wang and colleagues studied the transient response of single nanoantennas where a progressive cut obtained by using ion milling within the nanoantenna induces a highly sensitive tuning of the ultrafast nonlinear response associated with the transition from capacitive to conductive gap loading.[5] The excitation and control of ultrafast plasmons can also be used to design new spectroscopic tools. For example, Vogelsang and colleagues engineered photoelectron emission from the apex of a sharp gold tip illuminated via the grating coupling with few-cycle near-infrared light pulses. They demonstrated an efficient focusing of few-cycle plasmon wave-packets as compact sources of ultrashort electron pulses to perform time-resolved electron microscopy.[6]

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Nano Lett. XXXX, XXX, XXX−XXX

More recently, Tomita and co-workers used a similar approach to reach a background-free dual-wavelength nanofocusing of surface plasmons, enabling a selective pump−probe microscopy scheme with subdiffraction resolution.[7]

Plasmonics and nanophotonics also provide promising alternatives to overcome the fundamental limits of electronics, such as bandwidth and clock-time. Many recent advancements in this direction rely on the use of light as the information carrier, paving the way toward light-based technologies, which will have a fundamental impact in terms of reduced energy consumption and performance efficiency. All-optical modulation of light states (such as intensity, polarization, and phase) represents an important application of ultrafast optics to develop future nanodevices for all-optical data processing. Wang and colleagues have shown that by combining gold nanoparticles with a resonant photonic cavity, they could achieve an enhanced dynamic modulation of the system optical response exceeding 100% within a few picoseconds by using a light pumping fluence of less than 1 mJ/cm^2.[8] Similarly, Chen and co-workers combined coherent perfect absorption and standing-wave light fields to maximize the photon−plasmon interaction strength by exploiting the hybrid integration of plasmonic nanoantennas within a silicon photonic resonator, showing that this architecture enables an ultrafast tuning of photon−plasmon hybridization, including reconfigurable routing of the standing-wave modes.[9] Recently, Grinblat and colleagues showed that an ultrafast nondegenerate modulation of light properties can be achieved in the sub-20 fs scale in a hybrid metal-dielectric system supporting anapole modes.[10] Taghinejad and co-workers exploited the ultrafast dynamics of hot electrons at the interface of plasmonic metals and charge acceptor materials to achieve an active modulation of the phase, polarization, and amplitude of light through the nonlinear modification of the optical response of a plasmonic crystal that supports subradiant, high quality-factor, and polarization-selective resonant modes.[11]

An interesting landscape, which has been explored in recent years, is the possibility to control the ultrafast dynamics of polaritonic modes, such as excitons, using plasmons. Systems that would strongly benefit from this coupling are the so-called single photon emitters, such as quantum dots or fluorescent dyes. Single photon emitters are critical components in quantum information and computation, functional quantum circuits, and nonlinear single-molecule spectroscopy. Unfortunately, the intrinsic radiative lifetime of single photon emitters is typically on the order of tens of nanoseconds, thus limiting the maximum single photon emission rate, and consequently the entanglement probability rates. When coupled to plasmons, the decay time of a single photon emitter is drastically reduced and the total emitted power is increased, as demonstrated by Tran and co-workers.[12] Similarly, Hoang and colleagues demonstrated an ultrafast spontaneous emission on the order of 10 ps from a single colloidal semiconductor quantum dot coupled to a plasmonic nanocavity at room temperature, with a simultaneous increase of the total emission intensity by 3 orders of magnitude.[13] In addition, the single photon emission of fluorescent molecules can be drastically enhanced if these objects are integrated within plasmonic architectures. Schedlbauer and co-workers have measured, by using a femtosecond double-excitation photon correlation technique, a ∼75-fold radiative rate enhancement and fluorescence lifetimes down to 19 ps in a system composed of one donor and two acceptors, where a single dye molecule was positioned accurately between two gold nanoparticles using DNA origami.[14] In general, room temperature experiments involving single photon emitters focus mostly on efficient generation of single plasmonic modes. A simultaneous interaction of the emitter with multiple plasmonic modes would enable multiple functionalities in plasmonic circuits. Schörner and Lippitz have recently demonstrated an efficient nonlinear four-wave mixing mechanism based on the coupling between a single terrylene diimide molecule and the surface plasmon modes of two single-crystalline silver nanowires with an increased efficiency up to a factor of 50 compared to far-field excitation.[15]

Exciton−plasmon hybrid systems have also been proven to be very promising for next-generation nanoscale coherent lasing sources.[16] Hoang and co-workers have demonstrated long-range (∼1 mm) spatial coherence and ultrashort temporal coherence (∼2 ps) in lattice plasmon lasers based on periodic arrays of gold nanoparticles and a liquid gain medium at room temperature. Surprisingly, the long-range spatial coherence occurs even without the presence of strong coupling with the lattice plasmon mode extending over macroscopic distances in the lasing regime.[17] Deeb and colleagues have also demonstrated how nanolasing can be achieved in nanocavities down to the single unit of a plasmonic array.[18] The coupling of organic molecules and plasmonic systems is of great interest also from a fundamental point of view, shining new light also on nanoscale plasmon-driven chemical processes. Eizner and co-workers studied the temporal dynamics of strongly coupled exciton−plasmon polaritons in a system made of Al nanoantennas coated with J-aggregate molecules, displaying strong ultrafast nonlinearities, such as a periodic energy exchange between the organic exciton and the plasmon polariton mode within 14 fs, as well as plasmon−exciton hybrid ground-state bleaching.[19] Ramezani and co-workers explored a plasmonic cavity made of an array of metallic nanoparticles strongly coupled to organic molecules supporting Frenkel excitons, which are responsible for exciton−polariton condensation. Their study was the first direct experimental evidence that molecular vibrations drive condensation in organic systems.[20] The applications of ultrafast plasmonics to photochemistry in strongly coupled systems are also very wide. For example, plasmonic-mediated catalysis is poised to enable catalytic mechanisms not always attainable with conventional methods. Kumar and co-workers studied how the ultrafast hot plasmonic electrons transport can enable efficient photochemical conversion of CO_2 into formic acid, demonstrating that controlling ultrafast plasmonic processes allows for a rational selection of photoinduced reaction pathways.[21]

Another interesting perspective is represented by the progress in developing light sources and detectors in the terahertz (THz) region of the electromagnetic spectrum, the so-called fingerprint region of molecular vibrations. Advances in this direction rely on the development of THz light modulators. In this context, the pioneering work by Baig and colleagues introduced the first THz modulator combining broad bandwidth, picosecond time resolution, and large modulation depth for THz light intensity and phase modulation.[22] Moreover, the THz range is extremely important because at these frequencies electronic excitations can be coupled to lattice vibrations, as recently reported by In and co-workers.[23] Finally, an exciting research topic is the coherent all-optical control of electronic spins via ultrafast plasmon dynamics. The THz spectral range represents the missing piece to achieve a coherent coupling between the spin

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Nano Lett. XXXX, XXX, XXX−XXX

and plasmon wave functions. In this direction, Chekhov and collaborators have recently reported on surface plasmon-driven excitation of coherent spin precession with 0.41 THz frequency.[24]

In conclusion, the studies presented in this Virtual Issue point toward greater awareness and knowledge of how ultrashort light pulses interact with nanoscale matter through plasmons, especially in a regime where it would be possible to observe quantum phenomena at their typical temporal and spatial scales. In addition, the impact of ultrafast plasmonics on nanotechnology is multiple. For instance, in optoelectronics we can now fabricate nanodevices with high structural precision to manipulate single electrons using light pulses. We envision that in the near future ultrafast plasmon-driven electronics and quantum transport will be exciting research fields with a tremendous potential to revolutionize data processing and computing. We believe that our society, which is drastically evolving toward the Digital Age, will benefit from research efforts in this direction. Further, nanoscale systems supporting highly confined and enhanced optical fields may lead to fresh insights in fundamental mechanisms of light-driven chemistry such as in photocatalysis and photosynthesis, whose full understanding and control is still the main roadblock toward the synthesis of their efficient artificial counterparts. We are confident that studies along this path will increase in the years to come and disclose new routes toward practical applications of ultrafast plasmon-based nanochemistry.

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Notes

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Nano Lett. XXXX, XXX, XXX−XXX

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Nano Lett. XXXX, XXX, XXX−XXX