Multipolar and bulk modes: fundamentals of single-particle plasmonics through the advances in electron and photon techniques

Review article

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Abstract: Recent developments in the application of plasmonic nanoparticles have showcased the importance of understanding in detail their plasmonic resonances at the single-particle level. These resonances can be excited and probed through various methods, which can be grouped in four categories, depending on whether excitation and detection involve electrons (electron energy loss spectroscopy), photons (e.g., dark-field microscopy), or both (cathodoluminescence and photon-induced near-field electron microscopy). While both photon-based and electron-based methods have made great strides toward deepening our understanding of known plasmonic properties and discovering new ones, they have in general progressed in parallel, without much cross-pollination. This evolution can be primarily attributed to the different theoretical approaches driving these techniques, mainly dictated by the inherent different nature of electrons and photons. The discrepancies that still exist among them have hampered the development of a holistic approach to the characterization of plasmonic materials. In this review therefore, we aim to briefly present those electron-based and photon-based methods fundamental to the study of plasmonic properties at the single-particle level, with an eye to new behaviors involving multipolar, propagating, and bulk modes coexisting in colloidal nanostructures. By exploring the key fundamental discoveries in nanoparticle plasmonics achieved with these techniques, herein we assess how integrating this information could encourage the creation of a unified understanding of the various phenomena occurring in individual nanoparticles, which would benefit the plasmonics and electron microscopy communities alike.

Keywords: bulk plasmons; cathodoluminescence; EELS; localized plasmon resonances; multipolar plasmon modes; nanoparticle plasmonics; PINEM.

1 Introduction

In this short review, we critically present and analyze key advances in electron-based [1, 2] and photon-based [3–5] techniques for the study of plasmonic phenomena in individual nanoparticles, with the overarching goal to encourage cross-talk between the plasmonics and electron microscopy communities, which, it is safe to say, has been rather limited so far. Herein, we will present analogies and differences among the various methods, focusing not only on how they can be integrated to better understand currently known phenomena, but also, mostly, to explore new behaviors, such as the interplay between bulk and surface plasmons in colloidal nanoparticles. While we are aware the various important techniques do exist, especially within the optical framework, herein we will focus only on those methods that can indeed provide fundamental insights into the behavior of surface and bulk plasmons at the single-nanoparticle level. The analytical toolbox for the study of plasmons has grown steadily and significantly since the 1980s; the focus of these studies has been however directed toward electron-based techniques. Driven by our extensive work on gold nanostars with high shape anisotropy [6–9], and motivated by the numerous fundamental questions that have arisen during these studies, we focus here on recapitulating the most cutting-edge investigative tools available for single-particle plasmonics, classifying them in two main classes: on one side

[Correction added after online publication 23 September 2020: "Adapted with permission from a study by de Abajo et al. [65]." third line of the Figure 5 legend was changed to "Adapted with permission from a study by Feist et al. [64]."]

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those that allow the study of the local nature of surface-localized and bulk plasmon resonances (electron-based methods) [9], and on the other side the ones that reveal the collective nature of plasmonic resonances (photon-based methods). In this critical review, we bring together a decades-long progress in both classes, focusing on the most important results achieved with each technique and comparatively assessing the benefits and drawbacks of each of them. In particular, we focus on the results relevant to supporting the coexistence and interplay of localized and propagating polaritons in individual colloidal nanostructures, and on the interaction and coupling between surface and bulk plasmons within them.

We first provide a comparative review of electron-based and photon-based techniques, which have already been the focus of several reviews [10–13] and research papers [14, 15], and proceed back to the roots of plasmonics, which dates in the 1950s, where the concepts of local and nonlocal phenomena were first proposed. Within the two classes of tools just described, we then juxtapose four groups of techniques, based on their excitation (i.e., pumping) and detection (i.e., probing) mechanisms. Pumping and probing with photons (optical techniques), pumping and probing with electrons (electron energy loss spectroscopy [EELS]), or with combinations of both (cathodoluminescence [CL] and photon-induced near-field electron microscopy [PINEM]). We then focus on the description of a particular class of nanostructures, that is, those encompassing elongated, anisotropic features (e.g., gold nanostars), since our recent theoretical work appears to support the hypothesis that within them both propagating and localized plasmons can coexist [9]. In particular, these particles possess features (e.g., the spikes) that are long enough to allow the propagation of surface plasmon polaritons (SPPs) while being small enough as a whole to allow the formation of localized surface plasmons (LSPs). These high-aspect ratio features are also thin enough to allow probing of bulk and surface (interface) modes with comparable intensities. These interface and bulk modes (image-charge phenomena) are coupled in a Begrenzung manner [16], and in nanostructures with thicknesses comparable to the skin depth can be probed with the same experimental tools. Importantly, we suggest that, with the recent developments in both instrumentation and synthesis, the time might be right to propose a unifying picture for single-particle plasmonics, that takes into account both electrons and photons, and can be backed up by solid theory. While they might have not been until recently, our plasmonics and electron microscopy communities are now equipped with the analytical, computational, and theoretical tools to achieve it.

2 Exciting and probing: what kind of information can we harvest?

Although plasmonics is often described as the subfield of optics that focuses on light trapping and manipulation within nanostructured materials, the history of the field traces back to the idea of the electron cloud behaving as a Fermi–Dirac gas, when the local distribution is disturbed by a fast electron, leading to loss of energy and momentum [17]. This image of a plasmon being a collective interaction of a conduction-band electron gas resonating at the frequency of a fast electron was solidified by Ritchie in 1957 [17]. The idea of a plasmon as a collective oscillation of an electron gas had been introduced 5 years earlier (in 1952) by Bohm and Pines [18], who established the Debye length (see also Thomas–Fermi Screening) that dictated the locality limit of the net electrostatic effect of carriers in plasmas. Beyond the Debye length, the system behaves collectively as it would for an electron excited by photons of visible wavelengths, while in more proximal configurations within the Debye length the electron gas can be treated as a collection of interacting individual particles [18]. The configuration of an electron beam comparable in size with the Debye length has no analog in the case of a plasmonic system excited by visible wavelength photons and represents a challenge when comparing local plasmonic phenomena excited by photons with those excited by electrons. One obvious solution is to avoid the comparison in that regime and to utilize the aloof mode in an electron beam excitation. Firstly introduced by Batson and Treacy [19] in 1980, followed by Warmack et al. [20], the aloof excitation mode is slowly becoming the norm in nondestructive surface characterization of nanoparticles [21]. This approach involves a fast electron traveling in proximity to a nanostructure or film while its field interacts with the latter, similar to the field of a plane wave traveling in the same direction [11]. Nevertheless, as we will discuss in detail in the third section, nanoparticle plasmonics might hide a whole new world of excitations within the particle, namely those of bulk (or volume) plasmons that may not be detected this way [22]. Probing bulk plasmons in nanoparticles requires the subangstrom resolution of EELS [23] combined with the energy resolution of an aberration-corrected Scanning Transmission Electron Microscopy (STEM) [24]. It also involves the need of intersecting geometries [25], and it is hampered by the physical complications that arise from the accompanying damping of the plasmon [26]. These considerations will drive this section throughout the comparison between electrons and photons for plasmon excitation and probing.

Studying single-particle plasmonics via a correlative study of electronic and photonic excitations has been the focus of some review papers in the past [11] and recently [12, 13]. Herein, we focus exclusively on concepts and technical advancements that could help shape a unified understanding of phenomena that are still unclear or that, while known and understood in one subfield, have gone rather unnoticed in another. With this unifying rationale in mind, we address the relevant analytical techniques by organizing them in four groups, based on excitation and probing mechanisms: (A) exciting and probing with photons (optical techniques), (B) exciting with electrons and probing with photons (CL), (C) exciting and probing with electrons (EELS), (D) exciting with photons and probing with electrons (PINEM). We also focus on some of the latest advances, where pumping is leveraging the temporal features of a pulsed laser and the spatial accuracy of an electron beam.

In the rest of Section 1, we critically summarize what we believe being, to the best of our knowledge, the key techniques that can potentially realize this unifying understanding of single-particle plasmonics. In Sections 2, 3, and 4, we propose new directions in which these techniques could potentially contribute to establishing the fundaments for this holistic understanding. In Section 5, we conclusively present how some of the latest advances are pushing the limits toward this idea.

2.1 Exciting and probing with photons (optical techniques)

The two most widely used groups of techniques for the characterization of single-plasmonic nanoparticles involve the use of an optical microscope, an excitation beamline and a signal collecting spectrometer [27] and/or a probing secondary beamline, as thoroughly reviewed here [28]. Clearly described by Henry et al. [27] in their 2011 paper (Figure 1), and firstly introduced by Beversluis et al. [3] in 2003, this first group of techniques has been exploited in a plethora of studies. From exploring fundamental plasmonic properties [29–32] (key focus of this review), to clarifying the role of hot electrons in plasmonic photochemistry [33, 34] this relatively simple method is based on the following concept: as white light is channeled through a dark-field condenser, it excites plasmonic nanoparticles deposited on a substrate. The scattered light can be then collected by a camera, and the collected image is juxtaposed to an Scanning Electron Miscroscopy (SEM) micrograph to confirm the exact positions and shapes of the particles, or alternatively can be collected by a spectrograph. A slit ensures that the light from a single particle is analyzed and the scattered spectrum can be collected. This technique has become standard in the plasmonics community for single-particle characterization.

One of its main drawbacks is that it requires the use of a substrate, onto which the nanoparticles are spin coated or drop casted, which leads to a perturbation of the spectral profile of the particle due to particle-substrate coupling [35]. This technique is also diffraction limited and, while it does not allow the study of any local effects or shape-specific properties, it has been exploited for time-resolved measurements yielding interesting results [36]. To summarize, beyond the unparalleled advantages of this technique in allowing single-particle photon excitation and probing in short time scales, photothermal and hot electron regimes and particle-media interactions, its low resolution does not allow the detailed study of multipolar and bulk modes beyond their spectral fingerprints. For this we will not focus more on this group of techniques within this review.

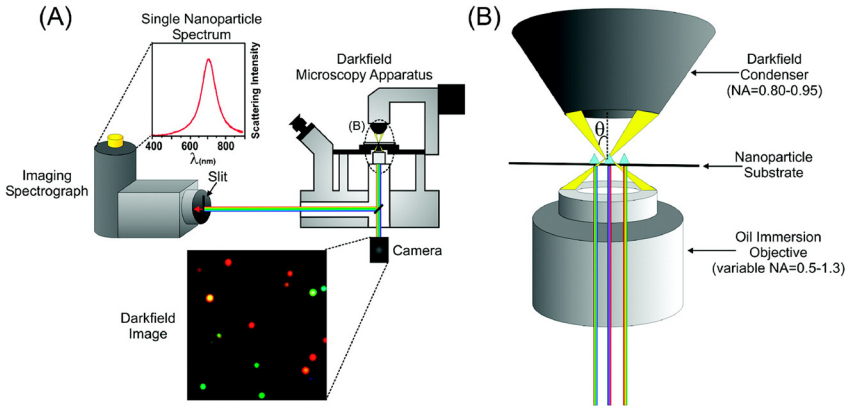

Figure 1: White light guided through a dark-field condenser excites plasmonic particles on a substrate. The scattered light is collected by a camera, and the image is then juxtaposed with an SEM micrograph for particle identification. A slit allows single-particle analysis. (A) Schematic of the beam path and the resulting imaging result. (B) Dark-field condenser and objective geometry and working principle. The field of view of the dark-field image shown is ~20 × 22 μm. Figure is reprinted with permission from a study by Henry et al. [27].

2.2 Exciting with electrons and probing with photons (cathodoluminescence)

In CL, electrons impinge on a material while the emitted photons, usually in the visible range, are collected and analyzed. As reported by Colliex et al. in their review of energy selective techniques [37], the plot in Figure 2 overlaps a wavelength-filtered and false color image with an SEM micrograph revealing the emission of GaN quantum discs embedded in an AlN nanowire. By scanning in two dimensions with an electron beam and measuring the emission at each spot, this technique tackles the diffraction limit problem with the high spatial accuracy enabled by the short wavelengths of the electron beam. Pushing the resolution to 1 nm [38], by employing a spherical aberration corrector and a field-emission gun, CL allows mapping of plasmonic modes [39] creating a detailed representation of the resonances. Recent advances have upgraded the technique to one of the most cutting-edge methods allowing time [40], angle [40–43], and single-electron measurements [44], rendering it, along with EELS (*vide infra*) a technique that truly pushes the boundaries of space and time resolution for the study of electron excited plasmons. One of the most useful tools in the CL family of methods is the employment of monochromatic [45, 46] and panchromatic [47] excitation. The latter is a rather old [48] method of CL imaging that averages the CL signal over all wavelengths that fall within the detection range. This is an obvious advantage against EELS, as the emitted photons of various wavelengths in CL provide a clear image of the optical behavior of the system under investigation, while the various energies of the inelastic scattering events in EELS cannot be identified with various photon wavelengths, as it is explained in the next part. An additional critical difference between EELS and CL is the mechanism of data acquisition. In CL, there are energy dissipation processes that occur in the beam-sample interaction volume, where excess carriers are regenerated, and it is the recombination of these carriers that generates each CL photon [49], while in EELS, the energy loss from the inelastic scattering events in the beam-sample volume is directly retrieved from changes in the same beam. This favors EELS not just in terms of spatial resolution accuracy but also in energy resolution [50].

2.3 Exciting and probing with electrons (EELS)

Although the oldest method in the plasmonics toolbox, introduced in 1944 [1], EELS still stands as an innovative and boundary-pushing practice owing to recent and ongoing developments in electronics and aberration correcting *modi operandi*. EELS utilizes the inelastic scattering of an electron with matter to provide spatial and temporal information on phenomena of electronic and acoustic nature occurring within it. In EELS-based studies of plasmonic phenomena, the short electron wavelengths of the Ångstrom-sized probe [52, 53] have allowed the detection of closely spaced resonating modes. The mapping capabilities developed using sophisticated software platforms revealed degenerate modes similar to the ones presented in Figure 3 from a recent work by Ringe et al. [51]. Diving into a sub-Ångstrom regime of resonances, of plasmonic nature and not [21, 54], EELS is truly advantageous as it also enables the visualization of their properties in the form of energy maps.

On the other hand, while the Debye length restrictions introduced earlier stand as a barrier toward a holistic understanding of plasmonic resonances, a few reviews have been shedding some light on this issue [11, 12]. For instance, it was found that, by juxtaposing the theoretical and the experimental information that describes the physical phenomena in electron and photon excitations, plasmonic hot spots are not only localized at the tips of nanostructures but also extend within the particles [11].

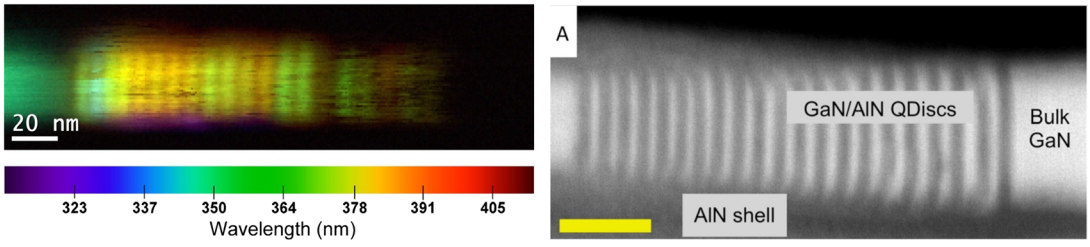

Figure 2: Overlapping a wavelength-filtered false color cathodoluminescence (CL) image with an SEM micrograph reveals emission from GaN quantum discs embedded in an AlN nanowire. Via a 2D e-beam scan and a respective emission measurement at each spot, the resolution limit becomes about 1 nm. Adapted with permission from a study by Kociak et al. [37].

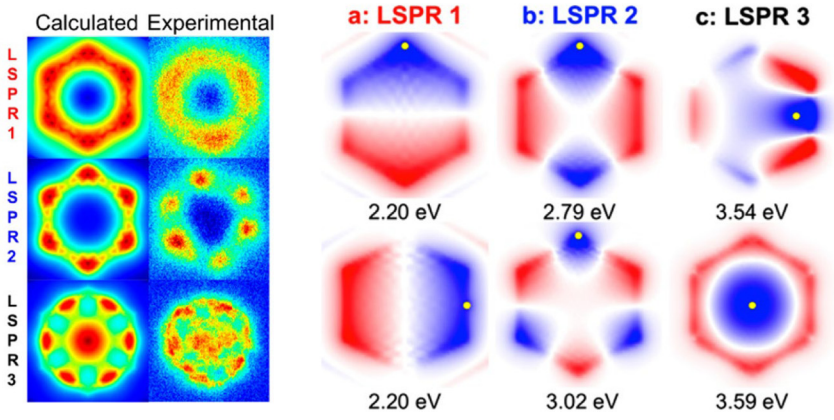

Figure 3: The mapping capabilities of electron energy loss spectroscopy (EELS) in comparison to modeling reveal degenerate modes in MgO nanoparticles from a recent work by Biggins et al. [51]. On the left, they provide the calculated and experimental intensity distribution for Mg nanoplates. On the right, the red and blue colors represent the opposite signs of the resonant perpendicular electric field allowing the location of two degenerate modes at 2.20 eV. Adapted with permission from a study by Biggins et al. [51].

Other studies also pointed out that, while most works consider one resonant eigenenergy based on the beam acceleration voltage, the local variation of the electron electric field excites multiple modes [12]. Beyond the possibility for multimodal excitation, an EELS probe is known to be bound to the Debye length restrictions for one more reason. It is referred to as the plasmon wake in an EELS excitation [55], which can be described as the electron carrying a longitudinal disturbance of the local charge density, consisting of a leading density enhancement and a following hydrodynamic wake. Even in the aloof mode [56], which adequately resembles a plane wave excitation, the information provided by a highly local electron beam has to be juxtaposed to a nonlocal photon beam study, as the two methods provide incomplete yet complementary pictures of the intrinsic properties of the system. Nevertheless, EELS is unsurpassed with respect to spatial and energy resolution and mapping qualities.

2.4 Exciting with photons and probing with electrons (PINEM)

Perhaps the most technically challenging technique in this list, and the newer one to be developed, PINEM has allowed imaging evanescent electromagnetic fields with electron pulses, given a spatiotemporal overlap of single-electron wave packets with intense optical pulses [58]. A momentum transfer between these optical pulses and the ultrafast electron packets allows for the mapping of the energy loss by the time-resolved electron beam, with the advantage of the short electron wavelength, resulting in a technique that combines the high spatial resolution of EELS and the high energy resolution of photon excitation. Introduced only recently in 2009, it has not yet been widely employed, likely due to its highly complex experimental nature and costs. Nevertheless, PINEM has provided the community with a few impressive results. For instance, it was leveraged by the Carbone group at École Polytechnique Fédérale de Lausanne (EPFL) to achieve the first visualization of the wave-particle duality of confined light on a nanowire [59] and by the Yurtsever et al. [57] at Caltech to directly visualize entangled particles (as depicted in Figure 4). Furthermore, by employing diffraction to extend the technique to the infrared [60] and by pushing the energy resolution to meV [61], these two groups have been providing the community with extraordinary insight into the studied phenomena.

A notable mention within this group of techniques is the normal incidence photoemission electron microscopy [62] that in 2014 allowed imaging SPPs. It would be very interesting to put it in use for single-particle plasmonic studies, especially considering the interplay between SPPs and LSPs, as we will be discussing in the next two sections.

2.5 Blurring the lines between electron and photon excitation and probing

A 2015 groundbreaking work by the Feist et al. [63], demonstrated the potential of ultrafast electron pulses (pushed in the attosecond regime) resulting from coherent manipulation of quantum systems with light, leading two years later to the demonstration of an ultrafast TEM that utilizes a laser-driven field emitter [64]. In other words, it realizes an electron pump consisting of a Schottky field-emission, laser-driven, electron gun and electron probe. Although the group has an impressively polymath record in plasmonic studies both experimental [65–67] and theoretical [68] alike, to the best of our knowledge, there has not yet been a publication on the study of single-particle plasmonics via their new UTEM (the operation principle of which is presented in the scematic of Figure 5).

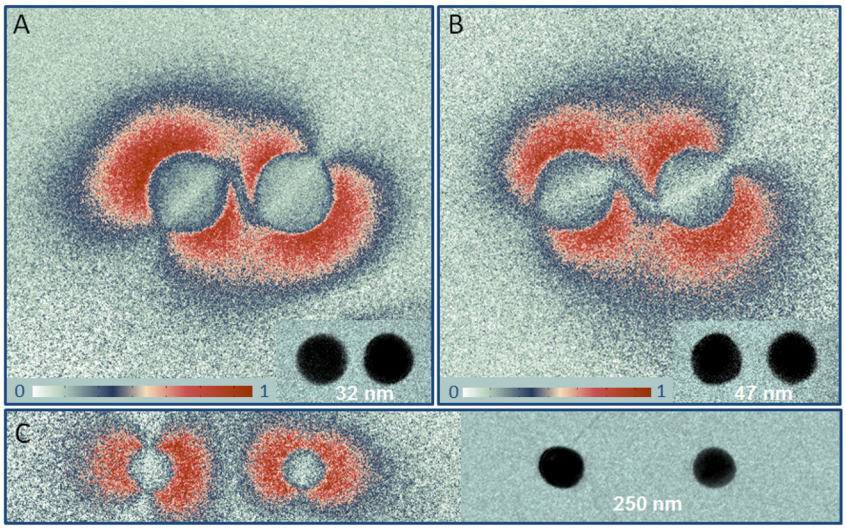

Figure 4: Photon-induced near-field electron microscopy (PINEM) employs a spatiotemporal overlap of ultrafast electron and optical pulses. Measuring the momentum transfer between the optical pulses and the electron ones, allows the energy loss mapping of photon-excited systems combining the high resolution of electron energy loss spectroscopy (EELS) and the photon excitation of cathodoluminescence (CL). Demonstration of nanoparticle entanglement by plotting the near-fields of a nanoparticle pairs at 32 nm (A), 47 nm (B), and 250 nm (C) with false color mapping. In 250 nm, interparticle distance, they exhibit dipolar-like fields, while at 32 and 47 nm a channel forms and their fields shape accordingly. Reprinted with permission from a study by Yurtsever et al. [57].

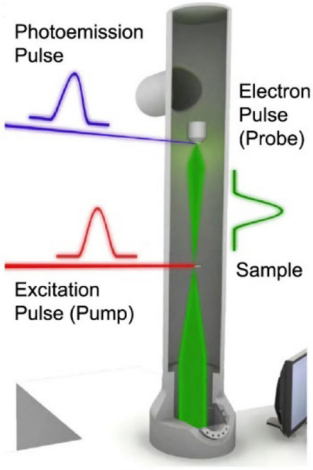

Figure 5: Ultrafast TEM (UTEM) realizes electron pump and electron probing by a quantum coherent optical modulation of the pump via an ultrafast laser. Adapted with permission from a study by Feist et al. [65].

3 Multipolar modes, plasmon standing waves, and the necessity of fast electrons

In this section, we compile the collective information gathered with some of the above techniques to focus on describing and understanding the interplay between localized and propagating plasmons [54], a new frontier of phenomena to be explored in individual plasmonic nanoparticles. This interplay was accurately described by electron microscopists as standing plasmon waves [69]. As most oscillatory behaviors in nature, this phenomenon can be usually described as a superposition of discrete modes. Therefore, we expect that most localized plasmons can also be treated as a superposition of standing propagating modes. In the convenient case of 1D isolated elongated structures as nanorods [70, 71] and nanowires [59, 72], our hypothesis seems to be supported and the image is pretty clear. However, in more complicated structures, such as the Mg nanoparticles reported in 2018 by Biggins et al. [51], one has to consider that any standing wave can be mathematically described as a superposition of two or more counter-propagating waves. Even if this suffices, the image becomes more complicated when we include the evanescent nature of the normal-to-the-interface component, that is, the contribution from the bulk component.

With a pure wave interpretation of a plasmon, if we consider a very thin plasmonic particle to be a 1D nanoantenna resonating at a single frequency and at the frequency-doubled eigenmodes, we can expect that, as the nanoantenna becomes thicker, the resonant eigenmodes will increase in full width half maximum and the various resonant bands will begin to merge. Similarly, the spectral profile of a thicker nanostructure can be seen as a superposition of a large number of eigenmodes of standing waves of interface charges. Not contradicting the multipolar image, the representation of plasmon resonances as superimposed standing polaritonic waves may lead to new discoveries and allow for a better understanding of the plasmonic phenomena. Combined with the interplay of bulk, localized, and propagating modes (*vide infra*), this approach might shed some new light into the (so far) unclear picture of bulk phenomena occurring in noble metals in the visible range. These metals are treated in the visible as selective plasmonic absorbers and electric field enhancers. Beyond this

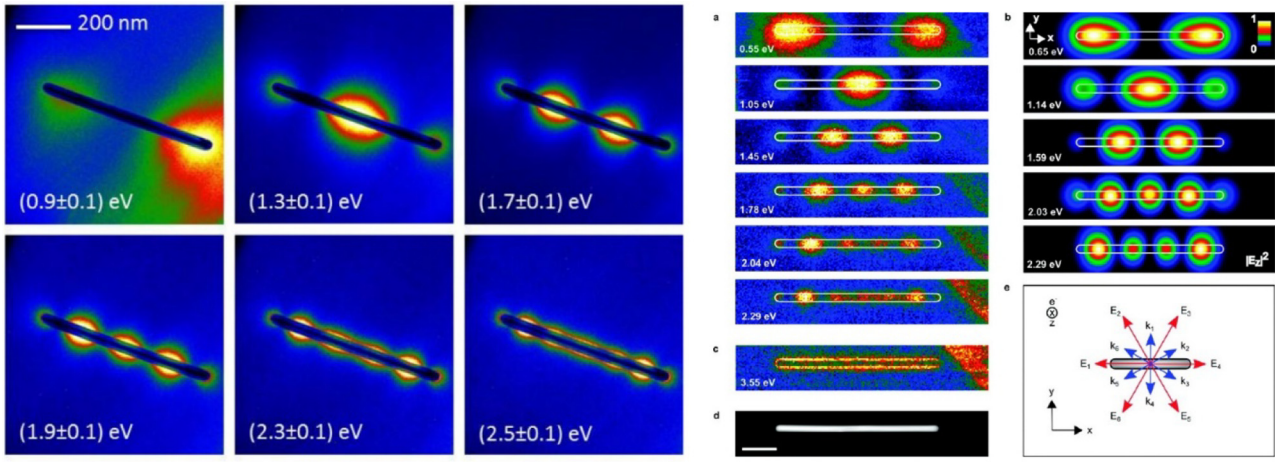

Figure 6: (Left) Treating silver nanorods as simplified 1D antennas, Nicoletti et al. [71] interpreted the harmonic eigenmodes of increasing order via electron energy loss spectroscopy (EELS) mapping. They simply called the probed modes as standing-wave patterns due to surface plasmon resonance. Reprinted with permission from a study by Nicoletti et al. [70]. (Right) In the same year, Rossouw et al. [72], working also on silver nanorods, confirmed these results with near-field simulated distributions. They called the probed modes as Fabry–Perot type modes with increasing order. Note the schematic of the geometry (right down) used for the near-field calculations. Photon-excited near-field intensities were integrated over multiple in-plane E vectors (6 shown) to achieve good agreement with experimental EELS maps. This is very nice way to describe the E-field properties of a point charge in an EELS excitation with many photon analogs. Reprinted with permission from study by Rossouw et al. [72].

dielectric function-centered view, we do not yet have a solid grasp on the phenomena leading to field enhancement, except in the case of simple systems, such as spheres or rods, and only at the surface. In addition, recent evidence supporting the existence of bulk plasmons in nanoparticles [73, 74], accompanied by older clear evidence of the same phenomena in different systems [26, 75] rationalize the need for further research in this area. Before delving into this subject in the next section, we focus here on some experimental evidence of the multipolar modes, that is, plasmon standing waves in elongated plasmonic nanostructures.

The work highlighted here reveals a collective behavior of standing waves of propagating modes, probed with different techniques. As EELS and CL reveal the modes [70–72] and their damping [76], PINEM introduces the simultaneous visualization of the wave-particle duality of photons. This evidence is a solid proof of polaritonic interference, visualized leveraging both classical and quantum mechanical understandings. Starting from this result, and reviewing the information previously obtained via EELS and CL, one can readily see the hypothesis of polaritonic standing waves shaping. This interpretation has been supported by the electron microscopy community for a while; we believe the subfield of plasmonics is now ready to support this common understanding.

By treating silver nanorods as a simplified 1D system, Nicoletti et al. [70] elegantly probed and interpreted their eigenmodes using EELS (Figure 6). In the same year, Rossouw et al. [72], working also on silver nanorods, confirmed these results with near-field simulated distributions, thus solidifying the hypothesis of the existence of higher harmonic mode confinement for polaritons in plasmonic nanorods (Figure 6). Exploring aluminum nanorods via CL, the following year Halas and Nordlander [71] identified higher harmonic polaritonic modes by comparing CL maps to Finite-Difference Time-Domain (FDTD) simulations, as reported in Figure 7. Equivalent and similar results have been presented from a slightly different standpoint by Bigelow et al. [15]. Plasmon EELS mapping results differentiating between longitudinal and transverse modes were presented a bit earlier in a sub-10 nm regime by Koh et al. [77] and eigenmodes of two Al sphere systems were presented quite earlier [79].

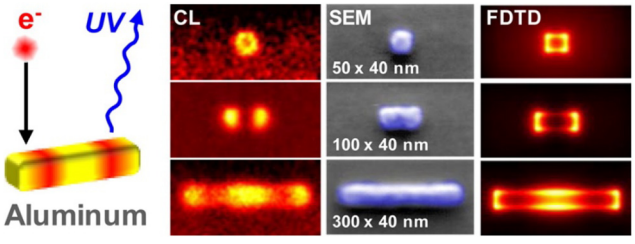

Figure 7: Probing aluminum nanorod near fields via cathodoluminescence (CL), Halas and Nordlander [71] identified higher harmonic polaritonic modes by comparing CL maps to FDTD simulations. They focused on the influence of the nanorod aspect ratio to the CL signal and the respective resonant pattern. Reprinted with permission from a study by Knight et al. [71].

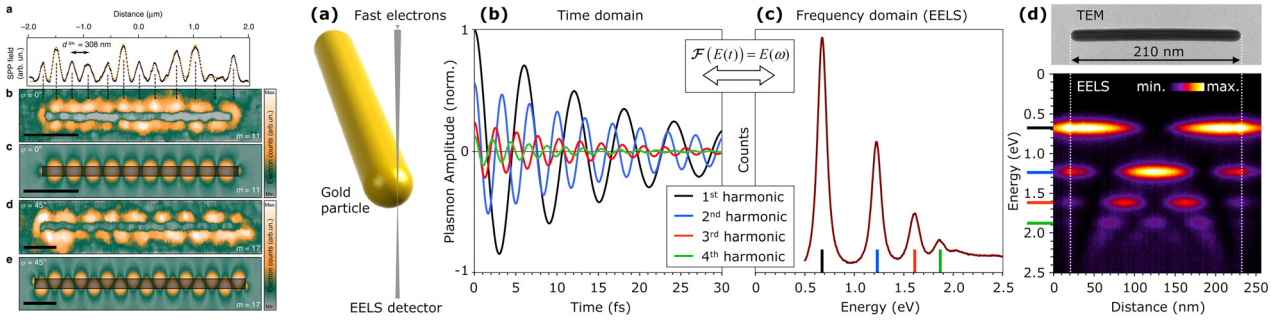

Figure 8: (Left) Quantum mechanical models predict very accurately the localization and interference of propagating polaritons forming standing waves. Piazza et al. [59] provided us with adequate evidence for the existence of propagating modes in long nanowires by probing the spatial variation of the interferometric surface plasmon polariton (SPP) field along the axis of a nanowire imaged above. Adapted with permission from a study by Piazza et al. [59]. (Right) The same phenomenon of trapped propagating plasmonic modes on nanowires was studied by comparing experimental data in the frequency domain to simulated time domain ones by Bosman et al. [70]. Each plasmon mode exhibits a well-defined spatial distribution of antinodes plotted here as a function of distance corresponding to an overlapped TEM image. Reprinted with permission by a study by Bosman et al. [76].

Beautifully showing that quantum mechanical models predict very accurately the localization and interference of propagating polaritons forming standing waves, the Carbone group [59] provided us with solid proof for the existence of propagating modes in long nanowires, as seen in Figure 8. By comparing experimental data in the frequency domain to simulated time domain ones, Bosman et al. [76] interpreted the same phenomenon from a slightly different viewpoint (Figure 8). Although not a solid proof of the temporal signature of these resonances, the theoretical approach and the accurate predictions of the modes contribute to supporting the findings on the nature of the polaritonic resonances.

Taking now the extra step, and treating nanorods (or even thicker nonelongated structures) as resonators for superimposed standing waves of SPPs, might bring about novel interesting perspectives for the plasmonics and the nanomaterials chemistry communities. In this respect, because of their focus on the temporal signature of these phenomena, work like the one from Bosman et al. [76] highlight the way to a deeper, more accurate understanding. Based on the evidence provided by this kind of work, we will probably be able in the near future to explore both the nature of these plasmonic resonances and the timescale of their creation and propagation. In this manner, a localized multipolar plasmon could be seen as a superposition of SPPs, such as occurs in elongated structures, or a Chladni-like pattern of superimposed standing SPPs on an arbitrarily shaped particle. The necessity of fast electrons arises as a way to achieve the maximum spatial resolution, and it might also be the key to unravel the time signature of these processes.

4 Focusing on locality: from the interplay of localized and propagating modes to bulk plasmons

As reported in 2014 by Lemke et al. [54], it is possible to directly experimentally observe the mutual coupling and coherent interaction of propagating and localized plasmons. Utilizing interferometric time-resolved photoemission electron microscopy they monitored the interplay between surface plasmon wave packets and plasmonic nanodot antennas. Achieving subfemtosecond temporal resolution and less than 5 nm spatial resolution, and monitoring the interaction of a plasmonic nanodot antenna with a propagating SPP, they provided the community with a very interesting insight into the time frame in which a localized plasmon is generated and dampened. Specifically, they followed the LSP decay into the SPP continuum by monitoring the periodic shift of the elliptically shaped intensity pattern of the SPP right when the incident SPP wave packet passes the nanodot. This work stands as a paradigm of an in-depth study of both the spatial and the temporal nature of a localized plasmon. Importantly, based on the theoretical predictions and experimental observations (Figure 9) of interacting LSPs and SPPs, the use of these experimental tools has the potential to lead to impactful discoveries in the near future. In the results of Figure 9 [54], the size of the nanodot allows us to clearly distinguish between the localized and the propagating behavior, but what would be the upper bound size limit for

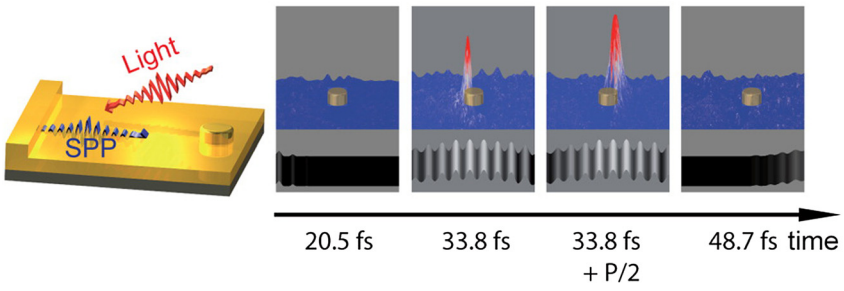

Figure 9: With a technique named interferometric time-resolved photoemission electron microscopy it is possible to monitor the interplay between surface plasmon wave packets and plasmonic nanodot antennas. Following the localized surface plasmon (LSP) decay into the surface plasmon polariton (SPP) continuum, one can monitor the periodic shift of the SPP intensity pattern when the SPP passes the nanodot as shown by Lemke et al. [54]. Reprinted with permission from a study by Lemke et al. [54].

LSPs and SPPs to be distinguished? Maybe the time has come for our communities to find out. Some work has already been pointing in this direction [79]. These studies could provide some interesting results to better understand hot electrons, or the role of hot electrons in the interplay between LSPs and SPPs [80]: perhaps we are sitting on the brink of a new subfield. By reviewing and reporting the most recent advances in the field with respect to the opportunity to employ them to study the existence of bulk or volume plasmons in single nanoparticles [22, 81], we realize the real potential of revealing new interesting phenomena by combining electron-based and photon-based techniques.

5 3D plasmon mapping and plasmonic particles as dual-cavities

After discussing the views of traveling, trapped, and bulk polaritons in localized plasmons, we propose a realistic unifying idea for these phenomena. To achieve this goal, we report on cutting-edge plasmonic mode mapping work carried out by two different groups of scientists using two different EELS approaches. In the first approach [82], presented in Figure 10, Camden et al. monitor in 2D the energy flow from plasmonic nanocubes to semiconducting substrates by juxtaposing EELS data and three-dimensional geometrical configurations of the particles under investigation. In a second approach, Nicoletti et al. [83] presented a different method, which incorporates tomographic tilt methods in a state-of-the-art EELS setup, to map plasmon intensities in 3D. Apart from the impressive capabilities of both techniques in mapping the plasmons in 3D, we would like to discuss the opportunity to extend these techniques to probe the bulk of the particles. According to what we have recently theoretically proposed [9], it is possible in some plasmonic metals (Ag, Au, and Cu), and especially in gold, for the bulk of the metal to sustain image modes of the surface ones, given some morphological constraints. These bulk resonances have been previously shown in various systems [84, 85], and it should be possible to map them in comparison to the surface ones, given the latest advances in EELS methods. Combined with the energy resolution and time resolution limits achievable today (*vide infra*), it will be groundbreaking to measure the coupling between plasmonic and nonplasmonic phenomena and to understand how these interactions jointly resonate with LSPs. The concept we proposed [9] of a dual-cavity system, with one cavity being the bulk and the other cavity being the interface of a plasmonic particle, could be realized by employing the capabilities of the methods highlighted here. The development of a unifying numerical model addressing both the electromagnetic interaction from a standing wave approach and the local charge density changes from, for instance, a density functional theory approach, can be beneficial towards this goal. As such method has not been applied yet to single-particle plasmonics, to the best of our knowledge, the opportunity to begin by experimentally verifying the simplest case is an attractive one.

6 Pushing the limits in energy and time resolution

Before, however, we argue for the need of new theory to understand what happens at the interface of a plasmonic particle and its surrounding media, we have to go back to how we can use the available methods to push towards a unifying understanding. In the following section we focus on some of latest work pushing the limits of energy detection and time-resolved measurements. By reaching the limits of achievable resolution with EELS for measuring the effects of an impinging electron that interacts inelastically with an MgO nanocube, Lagos et al. showed [86] that

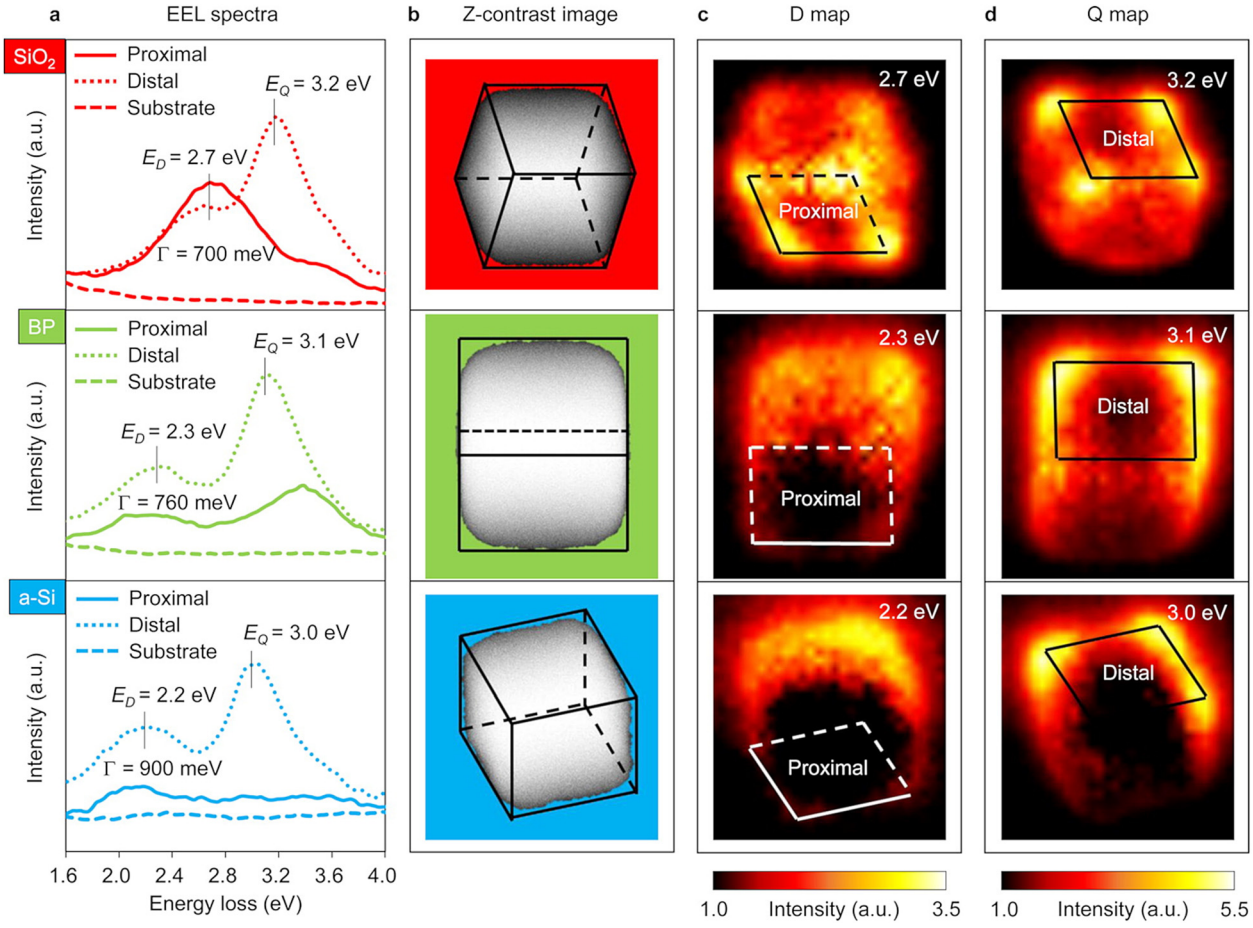

Figure 10: (Top) It is possible to monitor in 2D the energy flow from plasmonic nanocubes to semiconducting substrates via juxtaposition of electron energy loss spectroscopy (EELS) data and 3D geometrical particle patterns as shown by Camden et al. [82]. Reprinted with permission from Li et al. [82].

it is possible to map surface, edge, and bulk vibrational modes, as seen in Figure 11A, proving this technique to be an unsurpassed tool to unravel the coupling of a phonon bath with a dual cavity of bulk and interface polaritons. Importantly, they also showed how these plasmons release energy either as hot electrons or as radiative or conductive heat: Simply put, it is possible to monitor how plasmons dampen in time into acoustic vibrations. Vibrational EELS was introduced in 2014 [88] and has been proven an impressively useful tool for the damage-free study of biomaterials [88].

The work of the Zewail and Baum [89] have provided the physics community with invaluable understanding on the high-temporal resolution of electron dynamics [90] and the interaction between ultrafast optical fields and electron pulses [91–95]. Focusing on and understanding some of the latest work of Yakovlev et al. [96] on subcycle electron dynamics and electron pulse-phonon interactions [97] can provide the single-particle plasmonics field with a great potential for deeper understanding. However, the particle size (due to the appearance of higher order and collective modes) and the crystallinity (due to symmetry breaking from the presence of grain boundaries) limitations of the samples have to be considered always when applying condensed matter physics principles to plasmonic particles of several nanometers in size.

Time-resolved CL [98] (Figure 11B), reported in 2019 by Meuret et al. [99], is also a powerful tool to push the limits to understand the time fingerprints of plasmons while they are dampening. Along with the development of angle-resolved CL [43] and single-electron CL [44], the work of the Polman group represents one of the most cutting-edge approaches in single-particle plasmonics. Lastly, it is worth mentioning that a recent multigroup collaboration led by M. Aeschlimann has been pushing the study of the time dynamics of plasmonic systems to subfemtosecond limits [100].

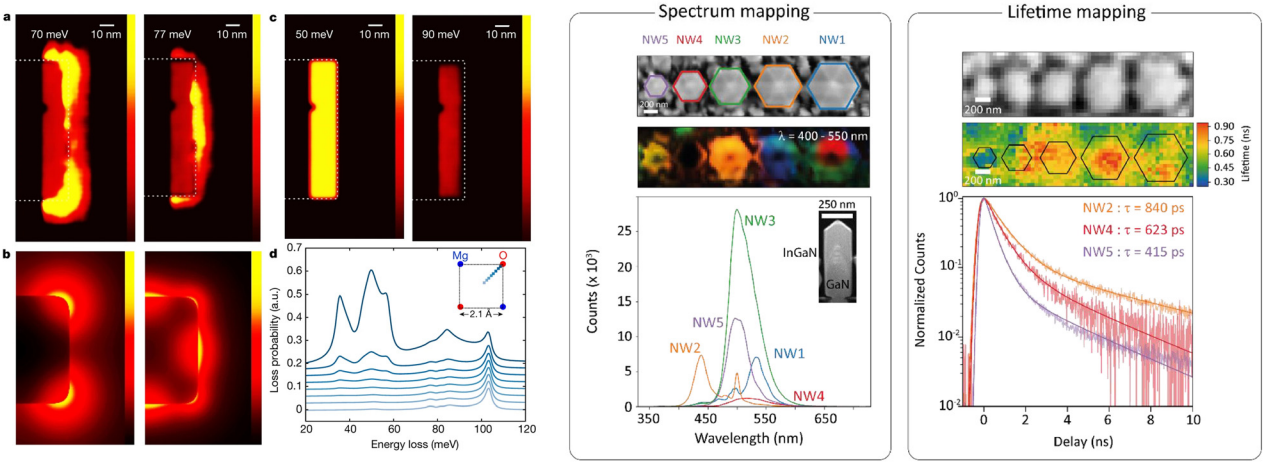

Figure 11: (Left) MgO nanocube surface, edge and bulk vibrational modes mapped by Lagos et al. [86]. Accompanying simulated electron energy loss spectroscopy (EELS) maps verify the nature of the modes. Simulated bulk EELS probabilities as a function of the probe position are plotted in the graph. Reprinted with permission from a study by Lagos et al. [86]. (Right) Time-resolved cathodoluminescence allows the plotting of spectral and lifetime maps for InGaN quantum wells embedded in an array of GaN nanorods as shown by the Pollman group. Adapted with permission from a study by Meuret et al. [99].

7 Conclusions

We provided herein a critical overview of how single-particle plasmonics can benefit from key advances in electron-based and photon-based techniques and the combinations of the two methods for excitation and probing. Guided by a focus on locality and nonlocality, the limitations, and the complementary information provided by the methods reviewed, we explored the concept of multipolar modes proposing that a treatment of plasmonic systems as standing wave polariton cavities could provide beneficial insight to the plasmonic community. We expanded our understanding within the interplay of polaritons and coupled localized phenomena, exploring the coupling of interface modes to their bulk counterparts into the existence of bulk polaritons. Driven by the latest advances in 3D mapping, time resolution, vibrational EELS, and time-resolved CL, we presented our view of a detailed image of nanoparticle plasmonics as dual-cavities of bulk and interface polaritons that couple and resonate and perhaps later on attenuate within phonon baths in measurable lifetime fingerprints. Given the ever expanding capabilities and always improving spatiotemporal resolution, there is enough evidence from the work presented here that we could soon be able to visualize the birth and attenuation of a plasmon on the surface and within a single particle.

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