Plasmonic quantum size effects in silver nanoparticles are dominated by interfaces and local environments

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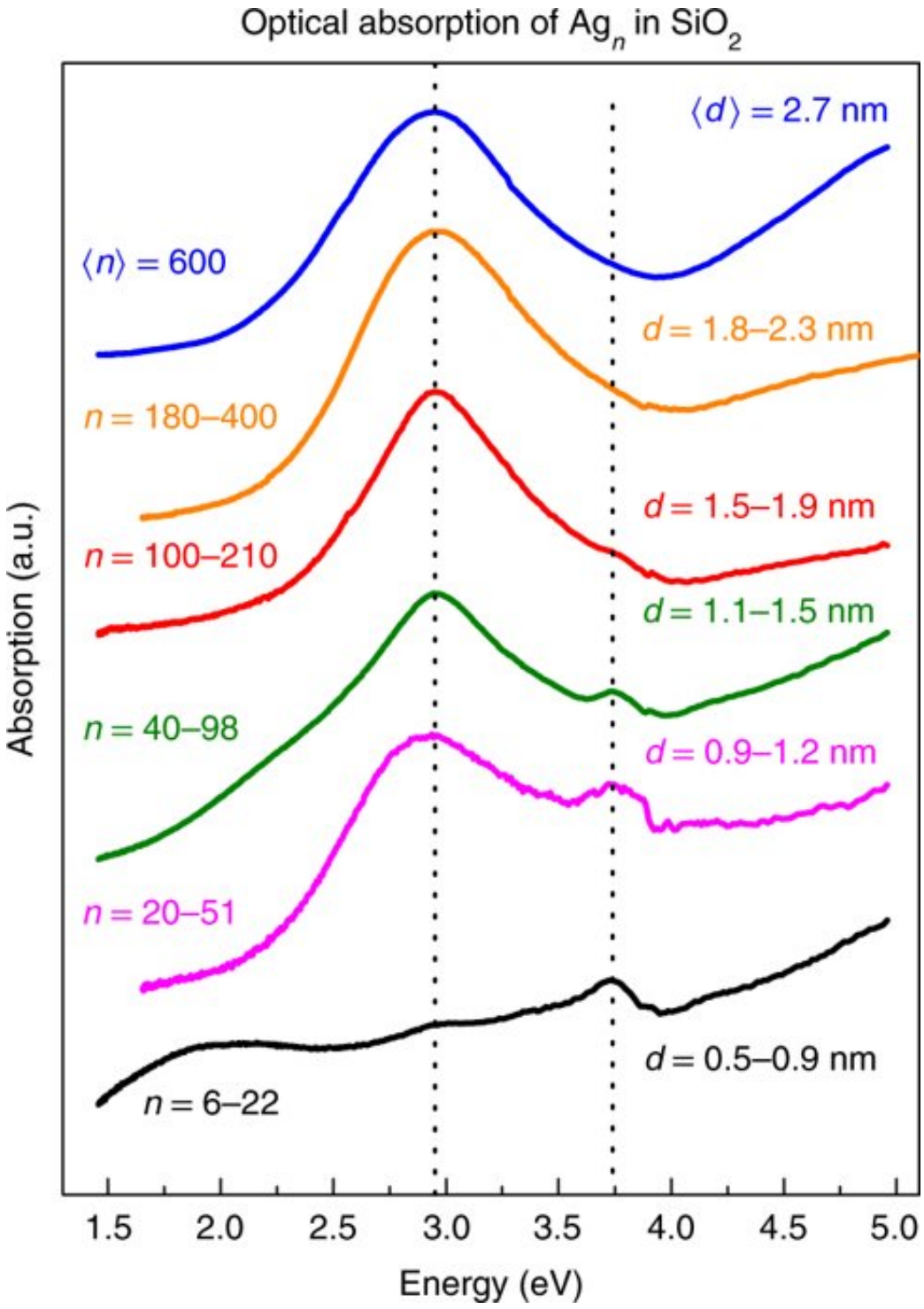


Optical spectroscopy. Optical absorption spectra for silver NPs of varying size, embedded in silica matrices. The topmost blue curve is for a non-mass-selected ensemble centered on a dimeter of d=2.7 nm, the other curves are for mass selected distributions. The minimal and maximal number of atoms per article transmitted through the mass spectrometer and the corresponding diameters are

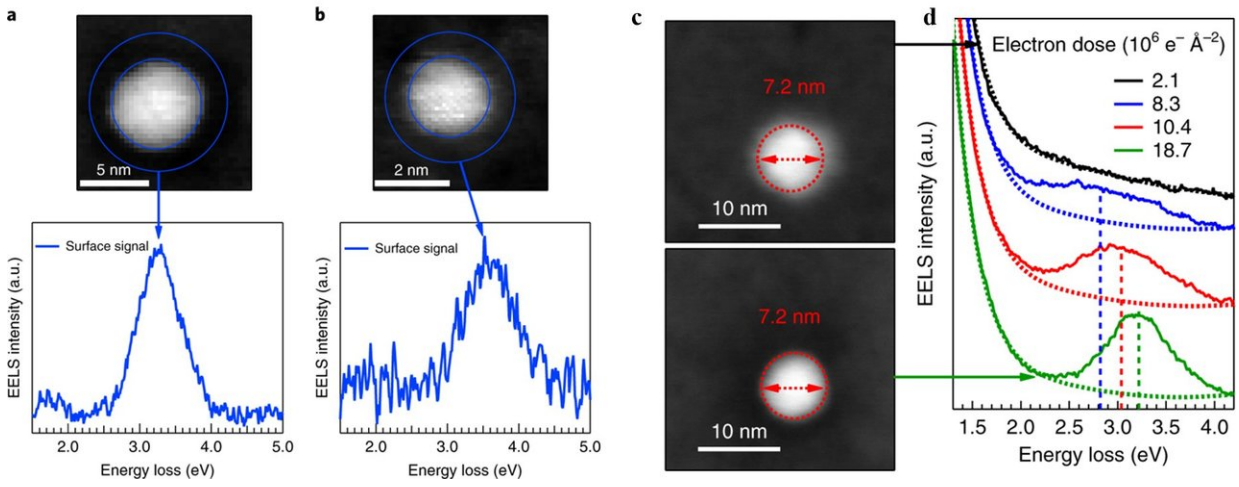
indicated. The broad signal around 2 eV for the smallest size is an artefact due to imperfect correction of Fabry- Pérot interference. The atomic peak at 3.75 eV for small sizes was attributed to fragmentation upon deposition. Credit: Nature Physics, doi: https://doi.org/10.1038/s41567-018-0345-z

When metallic dimensions are reduced to the nanoscale, a phenomenon termed localized surface-plasmon resonance (LSPR) appears due to electron oscillations, resulting in distinct optical properties suited for advanced imaging and sensing technologies. As particles approach the quantum regime with dimensions less than 10 nm in diameter, however, the existing knowledge of their properties becomes quite hazy. The plasmonic character depends on the collective electronic excitation that can be tuned across a large spectral range by adjusting the material's size and shape. Size dependent spectral shifts of the LSPR in small metal nanoparticles are induced by quantum effects, but the existing literature on the subject is quite controversial due to inconsistencies.

In a new study, Alfredo Campos and colleagues similarly report complementary experiments on size-selected small silver nanoparticles embedded in silica that yield inconsistent results on the same system. The quantitative interpretation offered by Campos et al. in the study was based on a mixed classical/quantum model that resolved apparent contradictions in the experimental data and in the literature. In the experiments, the scientists used optical and electron spectroscopy to investigate plasmonic properties of individual silver nanoparticles with dimensions reaching the quantum regime. The comprehensive model described the local environment as a crucial parameter that controlled the manifestation or the absence of quantum size effects. The results are now published in *Nature Physics*.

Understanding the electronic structure and optical properties of metal

nanoparticles is an extremely fruitful playground to develop quantum theories for metal nanostructures. Such systems have applications in catalysis, imaging and biosensing as well as in quantum optics for quantum information transfer. Improved single-particle experimental techniques have recently revitalized the interest in size-dependent plasmonic resonances in nanoparticles (NPs). For instance, electron energy loss spectroscopy in a scanning transmission electron microscope (STEM-EELS) is a particularly powerful technique that allows the mapping of spatial and spectral variations of different plasmon types at sub-nanometer resolution, where quantum effects can make the optical response more complex even for the simplest geometry. The technique can allow direct correlation between a particle's geometry and its plasmon resonance.

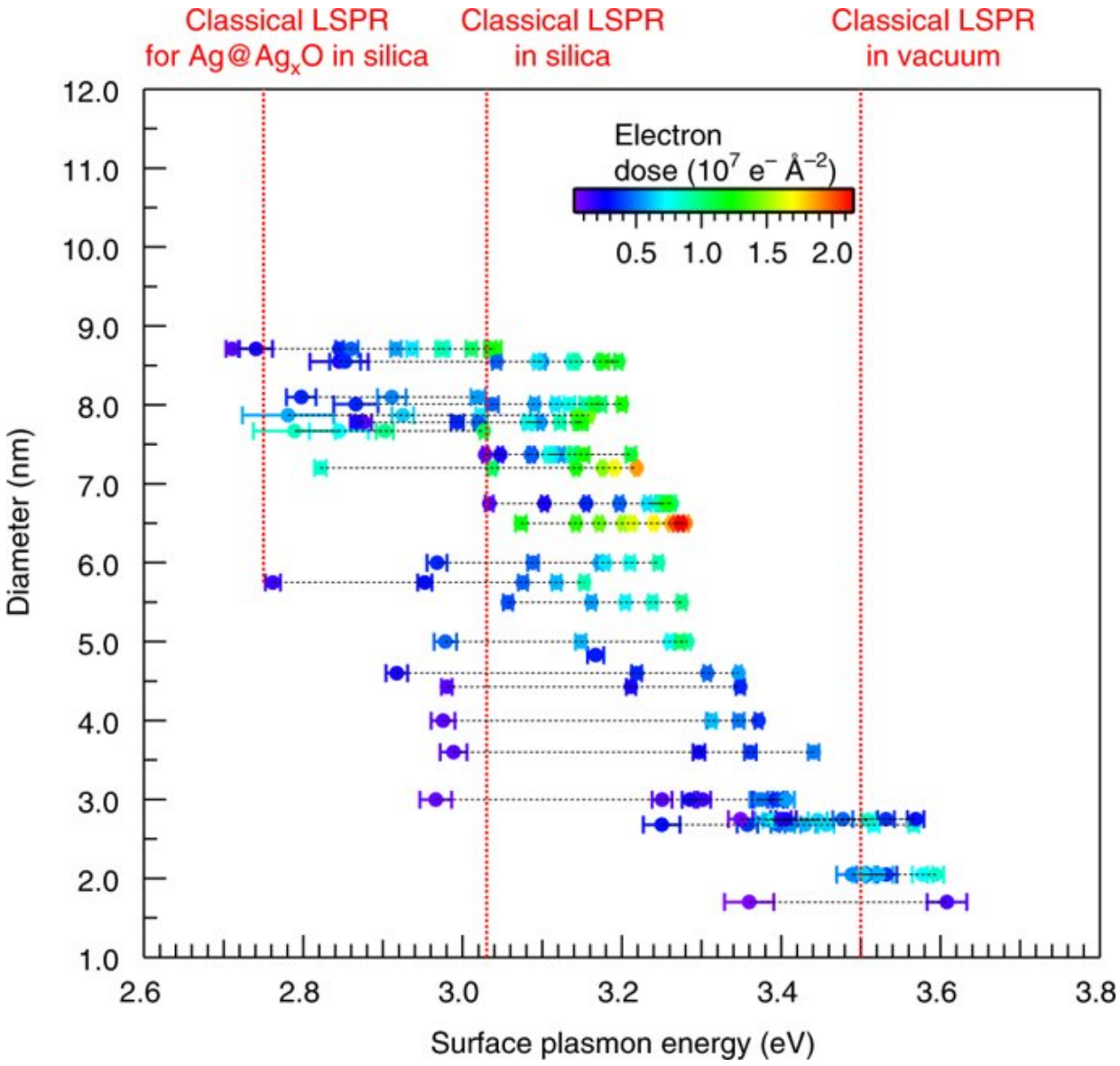


Electron spectroscopy and electron-beam-induced interface reduction. a) STEM images in high-angle annular dark-field (HAADF) mode of a 6.5 nm and a b) 2.0 nm particle embedded in silica. Bottom: EEL spectra associated with the surface signal (region of interest is between the blue circles). The contribution of the zero-loss peak is subtracted in the EEL spectra. c) STEM-HAADF images of a 7.2 nm silver particle embedded in silica at low and high electron doses. A diffuse layer related to silver oxide is visible at low electron dose and disappears

at a high electron dose. The diameter of the particle remains unchanged. d) Surface plasmon evolution with the electron dose. The curves have been shifted along the y axis for clarity. The contributions of the zero-loss peak and other background contributions to the EEL spectra are in dashed lines. Credit: Nature Physics, doi: https://doi.org/10.1038/s41567-018-0345-z

Previous studies showed a strong blue shift of the LSPR for silver nanoparticles fabricated with decreasing size using wet-chemical methods, in which the quantum plasmonic resonances were interpreted via semiclassical methods. Such interpretations remain controversial since the fundamental aspects of electronic spill-out (leading to a red shift) or influence of the surrounding matrix substrate were not considered. The similarity between electronic and optical observations were also only assumed but never derived for such small particles. As a result, the existing literature for small metal particles and their size-dependent plasmonic properties show large discrepancies that require clarification.

The authors first defined open questions linked to interpretations of the size-dependent shift of LSPR in small silver NPs. Then they used new, complementary experimental data to discuss experimental considerations in the study and proposed an interpretation using a quantitative theory. On this basis, they briefly addressed existing contradictions in the literature and focused on localized surface plasmons and not on the likewise observable - volume plasmons. In the study, the authors used a theory of a sophisticated electronic model in a dielectric environment to explain the trade-off that led to a red shift and a blue shift to establish a unifying approach for the optical and electronic properties of the unique system.



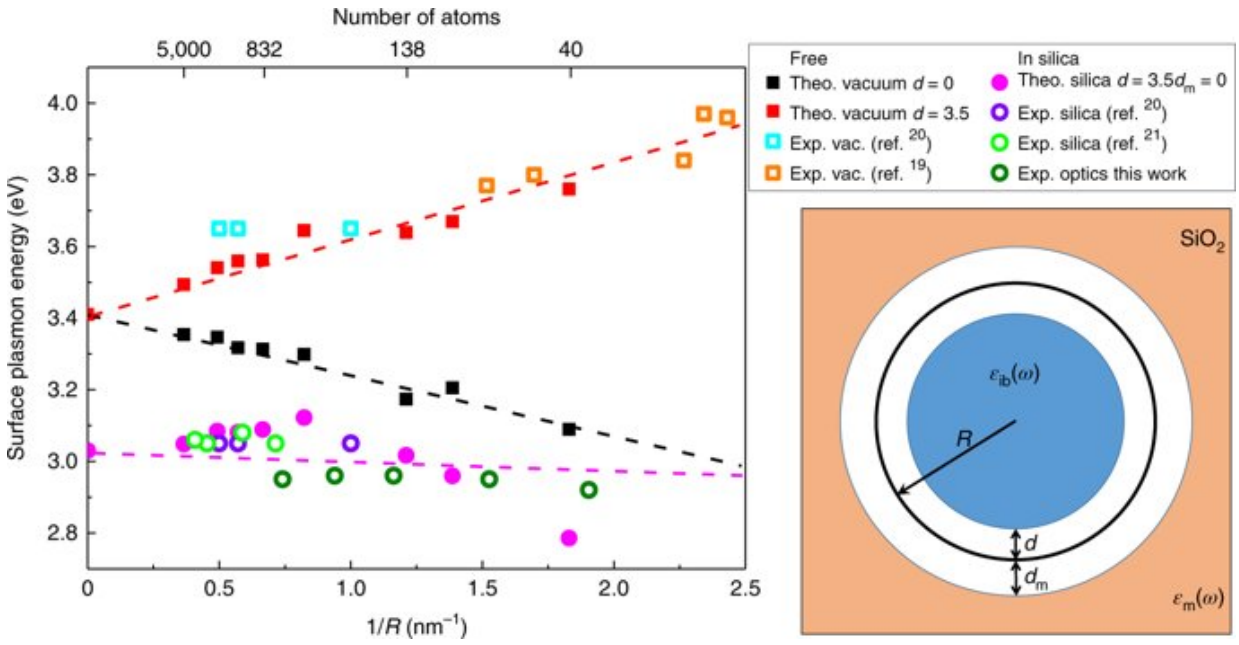
Electron-dose-dependent LSPR shift. Evolution of the localized surface-plasmon peak position of silica-embedded Ag NPs as a function of exposure time, indicated in a color code. The interaction with the high energy electron beam systematically shifts the plasmon to higher energies, the values for each particle being connected by a dotted line. The central and right vertical lines depict the classical (size-independent) values for the Mie plasmon of silica-embedded and free Ag NPs, respectively, in the quasi-static limit and calculated using previously reported values. The leftmost vertical line was obtained for the Mie plasmon of the core-shell and Ag-AgxO NPs at 75% oxidation ratio. Credit: Nature Physics, doi: https://doi.org/10.1038/s41567-018-0345-z

To overcome physical challenges that were previously observed with a chemically stabilized substrate and matrix effect, Campos et al. used physically prepared and size-selected pure silver particles and embedded them in a homogenous silica matrix. As a unifying approach, the researchers compared single-particle STEM-EELS measurements to ensemble-averaged optical microscopy experiments of the same system. In the study, experimental samples used for optical spectroscopy were approximately 1 μm in thickness, differing from samples used for electronic spectroscopy, approximating 30 nm in thickness.

Aside from the size variation, the scientists conducted single particle STEM-EELS experiments across a large range of thin samples fabricated under identical conditions as those used for optical spectroscopy. In the STEM-EELS experiments, images of silver NPs of 6.5 and 2.0 nm diameter were viewed alongside their corresponding EEL spectra for clearly visible strong dipolar surface-plasmon peaks at the particle surface combined with blue shifts between the spectra. Closer inspection of the data revealed greater complexity as the majority of NPs did not exhibit LSPR at the start of each experiment, as they were instead surrounded by a diffuse layer of silver oxide. The diffuse layer disappeared with knock-on collisions during continuous electron irradiation, leading to the observed LSPR peak and blue shifts. Under continuous energetic electron irradiation with increasing electron dose, lighter atoms were preferably displaced from the matrix and from additional oxygen at the particle interface. More and more matrix atoms were removed at higher electron doses under the beam leading to increased local porosity in the matrix and at the interface, observed as a trend with time in the study.

Values of the dose-dependent peak positions were obtained as a function of size, the LSPR data ranged between 3 eV to 3.6 eV. The results also

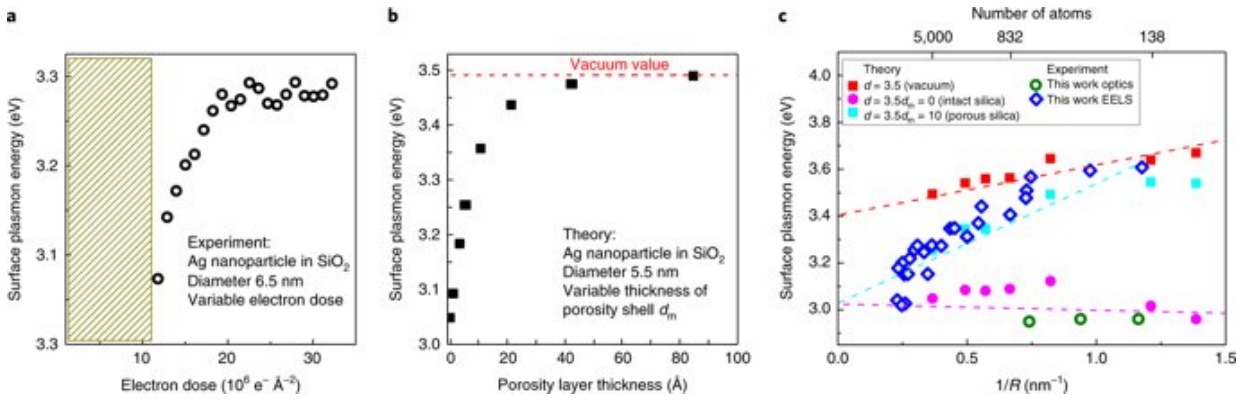
showed consistent red shifts due to the homogenous high-index silica environment, in agreement with previous results. The evolution of the size-dependent spectral position of the LSPR thus appeared contradictory for optical and electronic spectroscopy in the study.



Theoretical and experimental size dependencies. Size-dependent shift of the LSPR energy of Ag NPs in different environments. The solid squares are the calculated responses for particles in vacuum without (black) and with (red) the layer of reduced polarizability of thickness d (in bohr), compared to experimental values for bare silver clusters and silver cluster ions in the gas phase (open squares). The magenta solid circles show the theoretical values for silica-embedded Ag particles with the same layer of reduced polarization and a perfect interface (dm = 0). The intercepts at 1/R→ 0 correspond to the classical values of the dipolar mode for a sphere in the quasistatic limit. Open circles depict experimental values from optical spectroscopy for free and silica-embedded Ag particles. Dashed lines are guides to the eye. The insert at the right shows the concentric geometry used for the simulations of matrix-embedded NPs. For free particles, dielectric constant εm = 1 and thickness dm = 0. Credit: Nature Physics, doi: https://doi.org/10.1038/s41567-018-0345-z

Campos et al. resolved the apparent contradiction between optical and electronic spectroscopy to offer a comprehensive classical/quantum model framework that also clarified existing literature. The observed contradictions in the literature and in the study were not due to different experimental methods but due to different particle environments. The scientists introduced a self-consistent model to resolve existing theoretical and experimental contradictions in the study by accounting for all the important contributions in the system. These included 1) the electronic spill-out, i.e. extension of electronic density beyond particle radius in a non-infinite potential well, 2) the silver surface layer of silver nanoparticles with reduced polarizability, 3) the surrounding dielectric matrix including possible local porosity and 4) relevant finite-size quantum effects including non-locality of the electronic response.

The scientists showed that the spectral position of the LSPR (red and blue shift) resulted from a delicate balance between two counteracting quantum size effects (electronic spill-out and layer reduced polarizability). They observed that embedding the NPs in silica red shifted the LSPR due to the increased refractive index of the surrounding medium. The absence of any localized chemical covalent bonds between the metal and matrix were also noted, allowing the phases to retain their intrinsic properties without interference. The scientists formed a theoretical description which correctly reproduced optical experiments that included the matrix-induced effects. They found that the different sample thickness used for optical and electronic experiments that was expected to be a minor variation dominated the spectral response instead, changing the level of protection against oxidation and responses to irradiation - leading to the observed experimental discrepancies.



Plasmon peak shift. a) Experimental shift of the LSPR as a function of electron dose for a 6.5 nm particle. The shaded area corresponds to doses where no unambiguous LSPR signal was detectable in EEL spectra. After a minimal dose necessary for plasmonic activation, the peak blue-shifts by ~200 meV. The thickness of the initial oxide layer was ~1 nm. b) A qualitatively similar LSPR shift is observed in simulations as a function of vacuum layer thickness dm, here for a slightly smaller particle diameter. A value of thickness dm ≈ 5 Å results in a ~200 meV shift. c) Size dependence of the LSPR energy at high dose (like the saturated value in a), as dark blue open diamonds. For comparison are shown the calculated values for free (red) and for silica-embedded particles with either a perfect interface (dm = 0 bohr, pink) or a porous interface layer (mimicked through a vacuum layer of dm = 10 bohr (5.3 Å), light blue). Also shown are some of the data from optical spectroscopy of this work as open green circles. Dashed lines are guides to the eye. Credit: Nature Physics, doi: https://doi.org/10.1038/s41567-018-0345-z

The experimental trends were reproduced in calculations to provide a theoretical model that could quantitatively and consistently interpret the plasmonic response of free and embedded silver NPs. Using the theoretical model, Campos et al. were also able to explain the size-dependent spectral shifts observed in several previous experiments of embedded silver NPs as well, to resolve apparent contradictions in the literature. The scientists emphasized the importance of implementing all

relevant contributions of quantum-plasmonic systems as detailed in the study, paving the way for further studies of different plasmonic effects such as volume plasmons and in different systems such as nanoalloys.

More information: Alfredo Campos et al. Plasmonic quantum size effects in silver nanoparticles are dominated by interfaces and local environments, *Nature Physics* (2018). DOI: 10.1038/s41567-018-0345-z

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