Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Plasmons in Supported Size-Selected Silver Nanoclusters: Supporting Information

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SI-1. Coverage dependence of the Plasmon resonance

The investigation of size dependent effects of supported clusters with integral methods like optical spectroscopy demands a low surface coverage so that agglomeration can be excluded. In addition the plasmon resonance depends strongly on interparticle interactions if the distance between neighboring particles is too small[1,2]. The threshold value for our experimental setup was determined experimentally to be ~1×10^{13} cluster/cm^2, as can be seen in figure S1. For all measured cluster sizes the coverage was held below ~3×10^{12} cluster/cm^2 so that the observed shift of the plasmon energy can be assigned to intrinsic size effects explicitly.

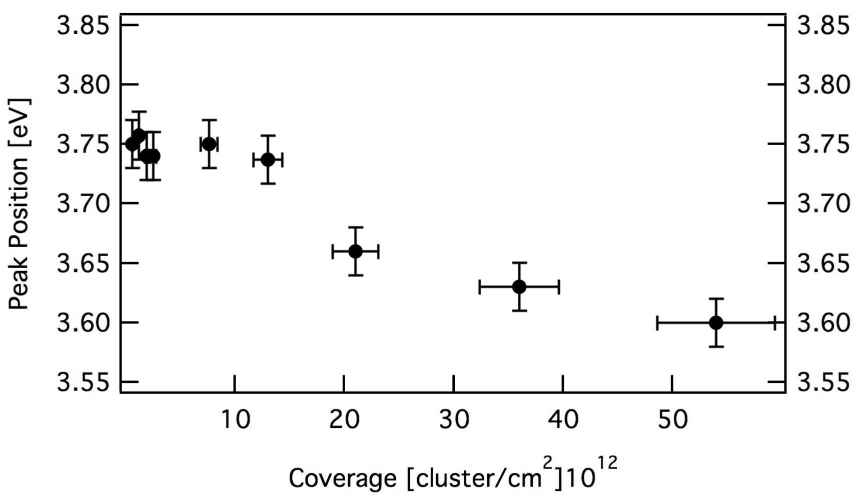

Figure S1. Shown is the position of the plasmon resonance of unselected Ag clusters supported onto BK7 glass substrates. The size distribution of the Ag clusters ranges from Ag_{21} to Ag_{65}. The weighted average determined experimentally is approximately Ag_{37}.

SI-2. Calculation of Cluster Size

Due to the size dependent nature of the plasmon energy the assignment of cluster sizes given as atoms/cluster to a particle diameter has to be done carefully. In the case of Ag clusters in the gas phase or embedded in weakly interacting rare gas matrices numerous data from calculations or diffraction measurements are available[3,4,5]. For reasons of simplicity the clusters are often treated as spheres and the particle diameter is expressed as $D = 2a_0r_sN^{1/3}$, where D is defined as the nominal particle diameter, N is the number of atoms in the cluster, a_o = 0, 0529 nm is the Bohr radius and r_s = 3,02 bohr is the atomic Wigner-Seitz radius of silver. In the case of supported clusters deposited from the gas phase, deformation of the clusters takes place during the deposition process and its not justified to treat the clusters as spheres[6,7,8]. Considering that s-SHG spectroscopy exclusively probes excitations perpendicular to the surface, the height of supported clusters is a good benchmark to assign the cluster size (atoms/cluster) to a diameter. STM measurements have shown that Ag_{55} clusters supported onto HOPG are 1.5 nm in height[9]. To the best of our knowledge this is the only STM measurement of size selected silver clusters within the size range investigated in this work. The predicted Wigner-Seitz radius of Ag_{55} clusters is 1.22 nm. Even though the supported Ag_{55} clusters are flattened, they are 0.28 nm higher than Ag_{55} gas phase clusters. This contradiction lead us believe, that 1,5 nm is the most appropriate assumption for the height of our Ag_{55} clusters, even though they are supported onto BK7 instead of HOPG. So we use 1.5 nm as a benchmark to correct the nominal particle diameter D of Ag_{55}. Under the assumption that within the investigated size range (Ag_{55}-Ag_9) the aspect ratio of the supported clusters is constant we used the same correction factor to calculate the height of our clusters and treated this value as the 'cluster-diameter'. Of course we are aware that the picture of flattened clusters with a constant axis ratio is just an assumption and despite strong cluster substrate interactions distinct lowest energy isomers may exist for different cluster sizes.

Table S1. Calculated cluster diameter using the measured height of supported Ag_{55} clusters as a benchmark.

Cluster Size [atoms/cluster]	height [nm]	1/D [nm^{-1}]
9	0.821	1.219
15	0.973	1.028
20	1.088	0.919
27	1.183	0.845
35	1.290	0.775
42	1.371	0.729
45	1.403	0.713
55	1.500	0.667

SI-3. Mie calculation

Following the classical Mie theory, the absorption cross section of a metal NP can be calculated using following equation:

Formula 1

$$\sigma_{i,ext} = \frac{\omega}{c_0} \cdot \varepsilon_m^{1/2} \cdot V_0 \frac{\varepsilon - \varepsilon_m}{(\varepsilon - \varepsilon_m) + \varepsilon_m}$$

where ω is the frequency of excitation light, c_o is the speed of light in vacuum, V_o is the particle volume, ε_m is the dielectric constant of the surrounding medium and ε is the complex dielectric function of the particle. To calculate the plasmon resonance of Ag particles with Mie theory we used the experimentally determined dielectric function of bulk silver[10]. The inhomogeneity of the surrounding medium is reflected by a mean dielectric constant ε_m = 1.65, consisting of 50% vacuum (ε_m = 1) and 50% BK7-glass (ε_m = 2.3). The choice of this mean dielectric constant of the surrounding medium is justified by the fact, that with s-SHG spectroscopy only oscillations perpendicular to the surface are probed[8]. Feeding this into formula 1, results in a plasmon energy of 3.25 eV as can be seen in figure S2. Note, that 1.65 is the upper reasonable limit for the dielectric constant ε_m. A decreasing influence of the substrate will shift the plasmon resonance to higher energies up to 3.5 eV, representing silver NPs surrounded solely by vacuum.

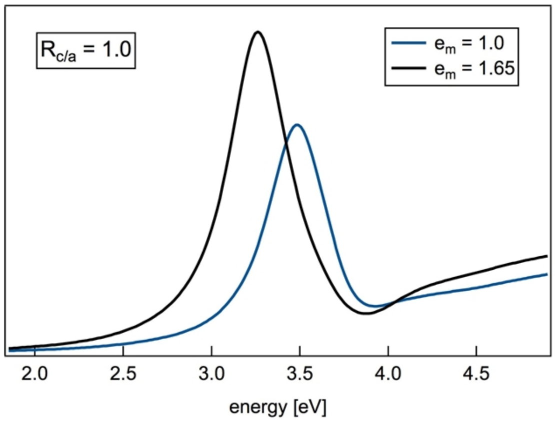

Figure S2. Calculated extinction spectrum of spherical silver NPs following classical Mie theory. Bulk values of complex dielectric function of silver were used. In blue, the extinction of free silver NPs (surrounded by vacuum, $\varepsilon_m = 1$) is shown. In black the extinction of silver NPs supported onto BK7 glass is shown, under the assumption that strate and vacuum contribute equally to the effective dielectric constant of the medium ($\varepsilon_m = 2.3$).

To account for variations from a perfect spherical cluster shape, classical Mie theory has to be extended by a shape parameter L_i.

Formula 2

$$\sigma_{i,ext} = \frac{\omega}{c_0} \cdot \varepsilon_m^{1/2} \cdot V_0 \frac{\varepsilon - \varepsilon_m}{(\varepsilon - \varepsilon_m)L_i + \varepsilon_m}$$

The mathematical expression of the shape parameter depends on the particle geometry, for an oblate spheroid with the three symmetry axes a = b > c it's values can be calculated as follows:

Formula 3

$$L_a = L_b = \frac{R_{c/a}}{2\left(1 - R_{c/a}^2\right)^{3/2}}\left[\frac{\pi}{2} - \tan^{-1}\left(\frac{R_{c/a}}{\sqrt{1 - R_{c/a}^2}}\right)\right] - \frac{R_{c/a}^2}{2\left(1 - R_{c/a}^2\right)}$$

Formula 4

$$L_c = 1 - 2L_a$$

In the case of Ag clusters, whose form deviate from a perfect sphere, 'plasmon-splitting effects' has to be considered. With a decreasing axis ratio $R_{c/a}$ (short particle axis / long particle axis) the oscillation across the short axis of the particle (in the case of an oblate supported particle this is the oscillation perpendicular to the surface) shifts to higher energies as shown in Figure S3.

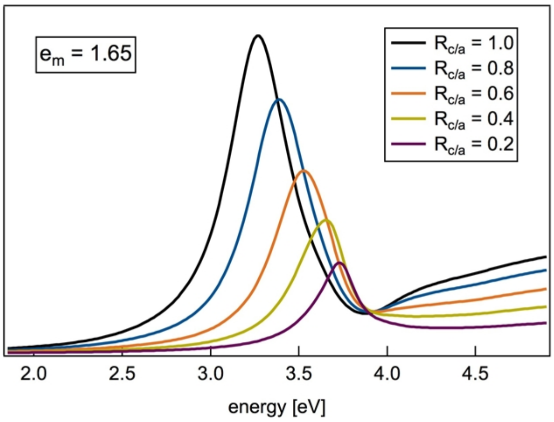

Figure S3. Calculated extinction spectrum of BK7-glass supported silver NPs with different axis ratios following formulas 2-4. The dielectric constant of the surrounding medium ε_m was set to the value of 1.65, corresponding to the mean dielectric constant of vacuum and BK7 weighted by 50% each.

An axis ratio of 0.2, which corresponds to extremely flat particles, shifts the plasmon energy from 3.25 eV to 3.72 eV. Hövel et al. determined an axis ratio of quartz glass supported silver nanoparticles with a mean diameter of 2 nm of 0.86[7]. Nilius et al. determined an axis ratio of alumina supported silver nanoparticles in the size range of 2-10 nm of 0.59[11]. Assuming a comparable axis ratio in the case of silver nanoclusters leads to a plasmon energy of approximately 3.4 eV, which is far away from the plasmon energies of BK7-glass supported silver clusters described in this paper. Even a combination of the smallest possible axis ratio and the smallest possible dielectric constant of the surrounding medium (ε_m = 1, corresponding to vacuum) can't explain plasmon energies of silver clusters above 3.76 eV, which is shown in Figure S4. This let us conclude, that the described blue shift of the plasmon energy of size selected silver clusters is caused by intrinsic size effects.

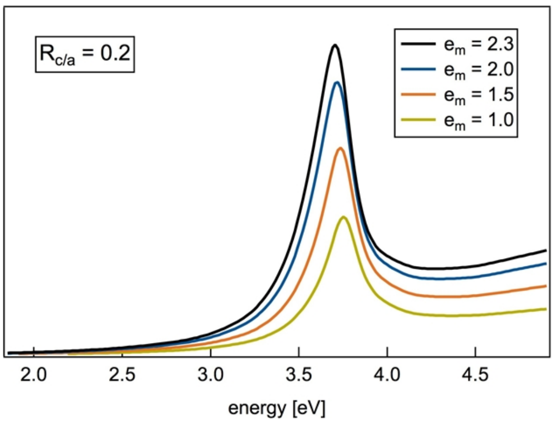

Figure S4. Calculated extinction spectrum of silver NPs with an axis ratio of 0.2. The dielectric constant of the surrounding meadium was varied from ε_m = 1 (corresponding to vacuum) to ε_m = 2.3 (corresponding to BK7-glass).

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