Supplementary Material:

Aspect-Ratio- and Size-Dependent Emergence of the Surface-Plasmon Resonance in Au Nanorods – an *ab initio* TDDFT Study

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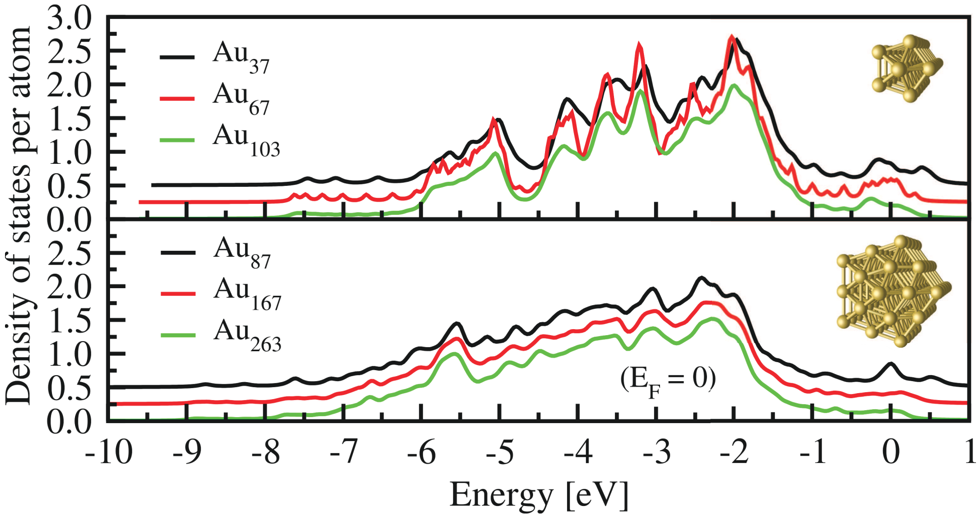

Figure S1: Density of states from the ground-state DFT calculation of the Au nanorods for constant width for three different values of the length, devided by the number of atoms. Upper panel: single-shell rods; lower panel: double-shell rods. The zero of the energy axis is the Fermi energy. A broadening of 0.1 eV has been applied. The curves are stacked for better visibility.

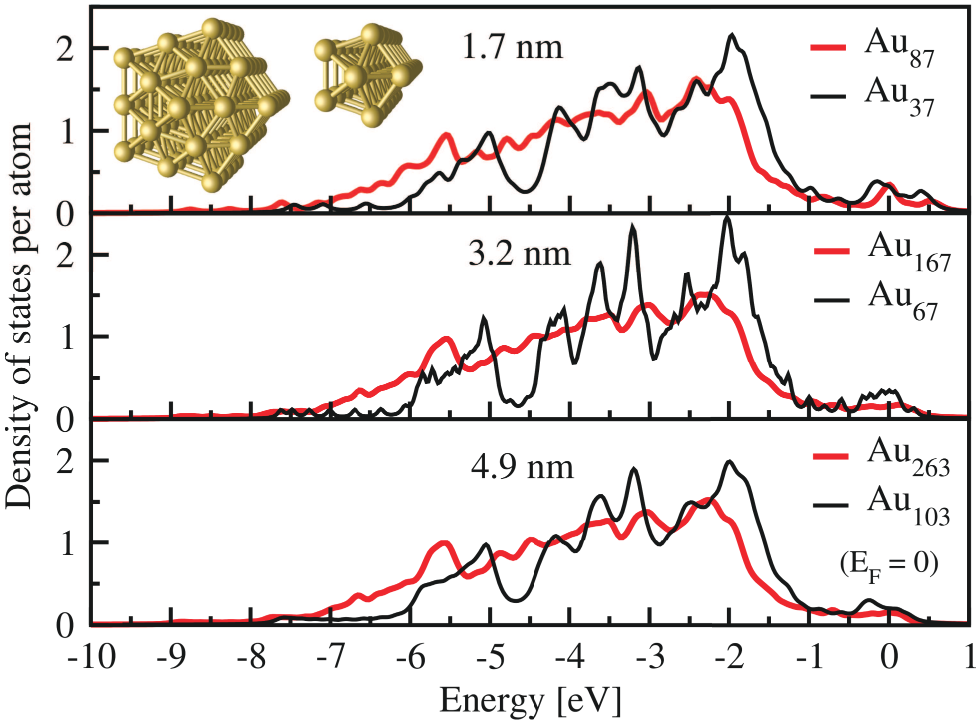

Figure S2: Density of states of the occupied states in the Au nanorods as in Fig. 1. For three different lengths, the DOS for the rods of two different widths is compared (red: double-shell rods, black: single-shell rods).

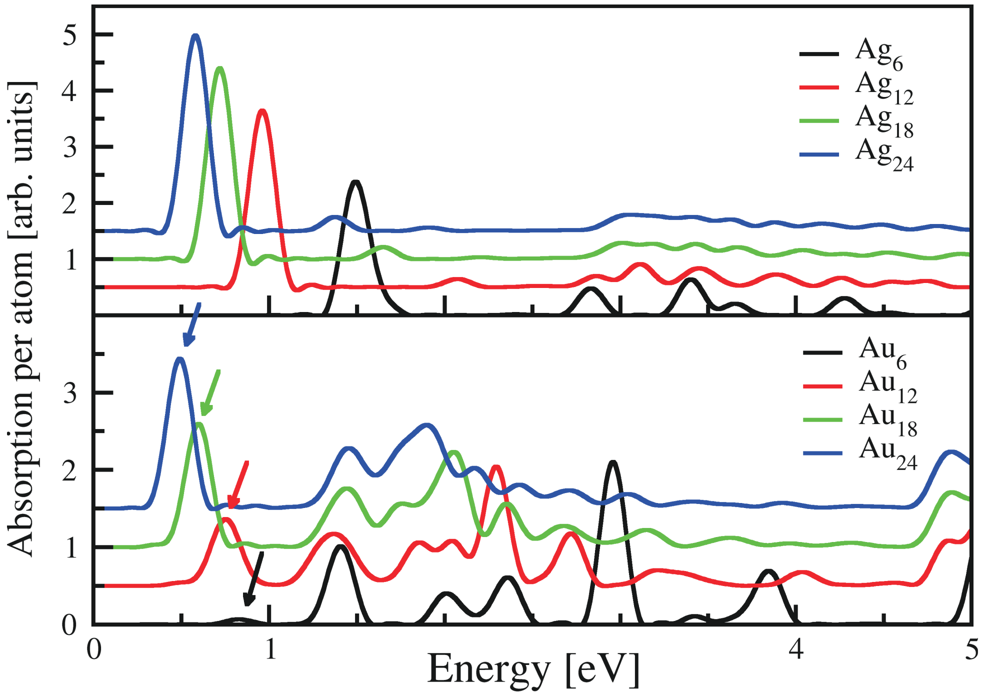

Figure S3: Absorption spectra of monatomic Ag$_n$ and Au$_n$ chains, n being the number of atoms, for excitation along the axis.

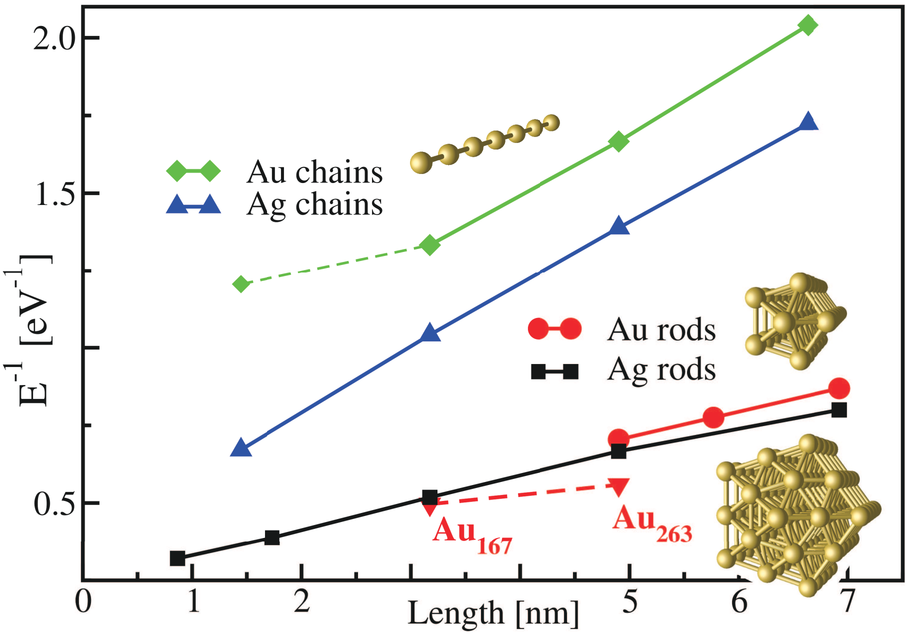

Figure S4: Peak energy of the longitudinal excitation for monatomic Ag and Au chains shown alongside the values of pentagonal Au and Ag rods as in Fig. [3] of the Communication. The dotted lines connect to points where the peak is not clearly defined.

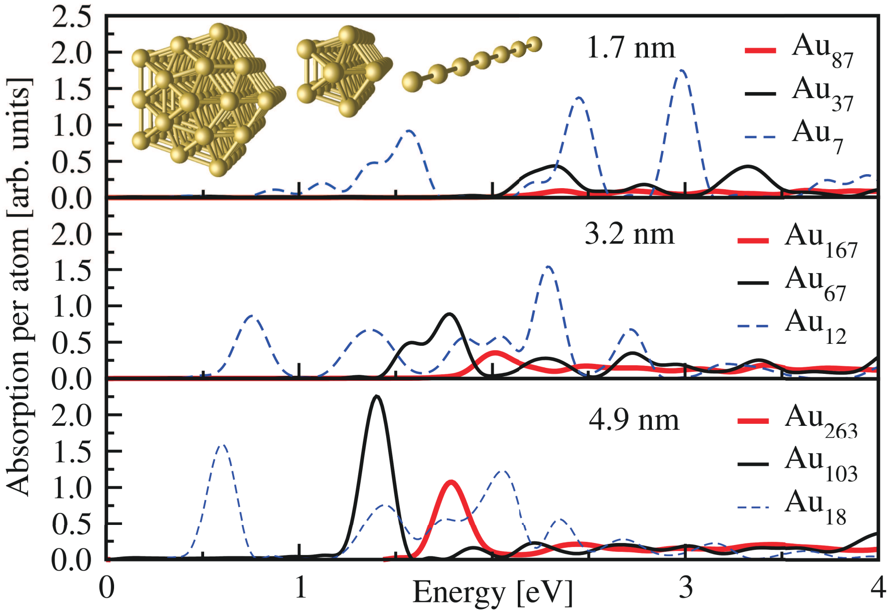

Figure S5: Absorption spectra for three different lengths of the nanorods as shown in Fig. [4] of the Communication. In each case, the spectrum of the monatomic chain (dashed) is shown alongside the two rods of different thickness. (Red: double-shell rods; black: single-shell rods; blue dashed: monatomic chains.)

Details of the Numerical Method

The optical absorption spectra have been calculated by time-dependent density-functional theory using the real-space code `octopus`.[1,2] The gradient-corrected PBE exchange-correlation potential was used. Norm-conserving Troullier-Martins pseudopotentials have been used which include the respective *d* electrons in the valence, that is, with 11 valence electrons for each atom. Relativistic effects are included as scalar relativistic correction in the radial part of the pseudopotentials. The spacing of the real-space grid was set to 0.18 Å for Au and to 0.20 Å for Ag. The radius of the spheres centered around each atom which make up the calculation domain was set to 5 Å. In this way, spectra are well converged up to about 5.5 to 6.0 eV.

Following a ground-state calculation, spectra are calculated using the time-evolution formalism in the standard way as proposed by Yabana *et al.* where at $t = 0$ a perturbation is applied. Technically, the wave functions are multiplied by a phase factor e^{ikz} that imposes a coherent velocity field and causes a dipole moment to develop as the system evolves freely.[3] We calculated the response for a perturbation in the direction parallel to the rod axis. The absorption spectrum is obtained as the Fourier transform of the time-dependent dipole moment.[2,3]

In our calculations, the time step for the propagation was set to 0.00158 fs for Ag and 0.00197 fs for Au. The total energy is used to monitor the stability of the propagation. The propagation time was 25 fs, and the Approximated Enforced Time-Reversal Symmetry (AETRS) propagator[4] as implemented in octopus code was used.

Influence of the choice of the exchange-correlation functional

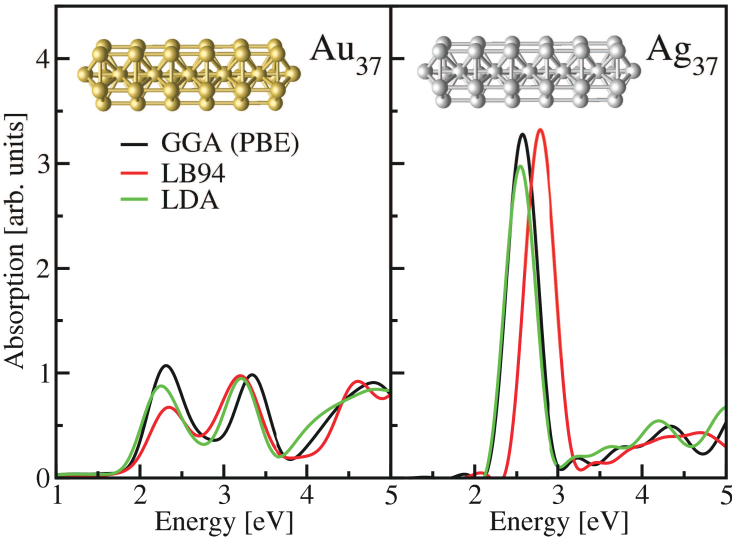

Figure S6: Absorption spectra for excitation along the rod axis for Ag_{37} and Au_{37} using different exchange-correlation functionals.

In Fig. 4 we compare the absorption spectra of the Ag_{37} and Au_{37} rods, using LDA, the GGA PBE, as well as the asymptotically corrected LB94.[6] The main conclusion from these results is that the difference between (short) Au and Ag rods is clearly represented by any of these functionals.

Comparison with Transition-Based Calculations

In Fig. 5 we show the comparison of our time-evolution results for a Au_{20} tetrahedron with the results calculated by Aikens and Schatz using Casida's transition-based approach.[5] The agree-

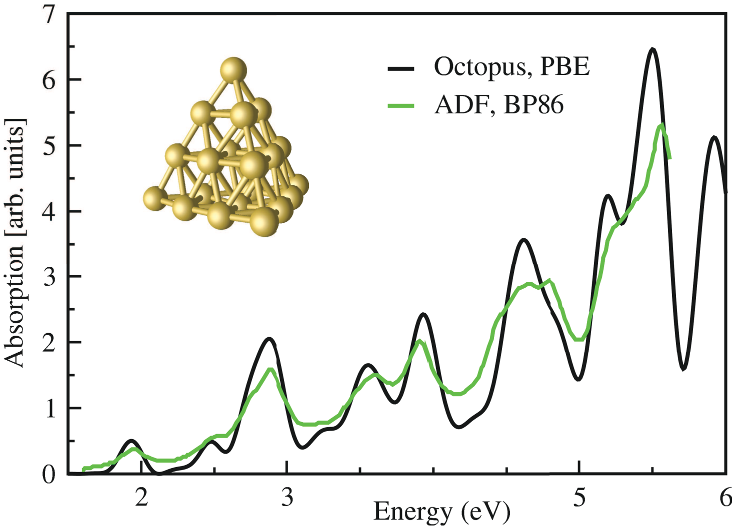

Figure S7: Absorption spectra of Au_{20} tetrahedron. We compare a calculation with the octopus code, using the present numerical set-up, with a calculation from Ref.[5]

ment between these two calculations is very good, although technically, the calculations are rather different. In addition to the difference real-time evolution vs. transition-based method, we use pseudopotentials, while Aikens *et al.* used localized basis sets. We include relativistic effects as scalar realtivistic correction in the pseudopotential, while Aikens *et al.* use ZORA. Different GGAs have been used.

References

(1) Marques, M. A.; Castro, A.; Bertsch, G. F.; Rubio, A. *Computer Physics Communications* **2003**, *151*, 60 – 78.

(2) Castro, A.; Appel, H.; Oliveira, M.; Rozzi, C. A.; Andrade, X.; Lorenzen, F.; Marques, M. A. L.; Gross, E. K. U.; Rubio, A. *physica status solidi (b)* **2006**, *243*, 2465–2488.

(3) Yabana, K.; Bertsch, G. F. *Phys. Rev. B* **1996**, *54*, 4484–4487.

(4) Castro, A.; Marques, M. A. L.; Rubio, A. *The Journal of Chemical Physics* **2004**, *121*, 3425–3433.

(5) Aikens, C. M.; Schatz, G. C. *The Journal of Physical Chemistry A* **2006**, *110*, 13317–13324.

(6) van Leeuwen, R.; Baerends, E. J. *Phys. Rev. A* **1994**, *49*, 2421–2431.