SUPPORTING INFORMATION

Valence Electron Density-Dependent Pseudopermittivity for Nonlocal Effects in Optical Properties of Metallic Nanoparticles

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Finite-difference time-domain

The absorption spectra of core-shell model are calculated by 3D FDTD using MIT Electromagnetic Equation Propagation (MEEP) simulation software package[1-3]. The simulation region is inside a cubic space with an edge-length of 20 nm, and a 10-nm-thick perfect matched layer is added at each face. A Gaussian-pulse source is used, and the width of the Gaussian source ranges from 1 eV to 5 eV. The resolution of the simulation in space region is 0.2 Å and the corresponding Courant factor is 0.5.

Quantum atomistic model by DFT

The ground state density functional theory calculations of nanoparticles were done by real-space code octopus[4-5] using PBE exchange-correlation potential[6-7]. For NaNPs, norm-conserving Troullier-Martins pseudopotential has been adopted in SIESTA format[6]. The maximum angular momentum considered is l = 0, such that only the one s-band electron is considered as the valence electron each sodium atom. The simulation box of is a real-space spherical region with a radius of 20.0Å, and spacing of the was set to be 0.20Å. The convergence criterion can be met if change in

relative electron density is less than 10^{-7}. To ensure spherical symmetry of electron clouds, only NaNPs with magic numbers of atoms are studied (92, 138, 198, 268, 338, 440…), and these kinds of nanoparticles are also referred as closed shell clusters[8-10]. For AgNPs, norm-conserving Troullier-Martins pseudopotential in SIESTA format has also been used. The d-electrons are included in the calculations, such that each silver atom contains 11 valence electrons, with one s-band electron and ten d-band electrons. The magic number of AgNPs to achieve closed shell clusters is slightly different from that of sodium[8] (35, 41, 59, 93, 139, 199, 269, 441…)

Quantum jellium model by DFT

For jellium spheres[11-12], their ground state density functional theory calculations were also done by octopus with LDA exchange-correlation potential.

Norm-conserving jellium pseudopotential has been used. The radius of the jellium sphere is defined as

$$R_{jellium} = R_s * N^{1/3} \quad \text{(S1)}$$

In the eq S1, N is the number of sodium atoms contained in a jellium sphere. The Wigner–Seitz radius,[13] R_s, is 4.00 *Bohr* for sodium atoms and 3.01 *Bohr* for silver atoms, each atom owns one s-band free electron, while other valence electrons are not included in jellium model.

The simulation box of is a real-space spherical region whose radius is 8.0 Å larger than the jellium sphere under study, and spacing grid being 0.20 Å. Convergence criterion is 10^{-6} in change of relative electron density. The simulations of nanosphere monomers were conducted in 3D mode and nanowire dimers done in 2D mode.

Absorption spectra calculation within TDDFT

The absorption spectra of atom clusters and jellium spheres are calculated by real-time time dependent density functional theory using real-space code octopus as well, based on previous ground state calculations.

A delta pulse was set to act as the external electromagnetic perturbation, and the time propagation for this incident wave was calculated. The propagation of the delta pulse was treated using approximated enforced time-reversal symmetry[14] (AETRS) implemented in the real-space code octopus. The time step of this propagation was set to be 0.000827 fs, and the total propagation length was 20000 time steps.

Extreme Learning Machine

In free electron density profiles at shell regions of NaNPs and AgNPs has been calculated by ground state DFT for particles contains no more than 833 free s-band electrons. For NaNPs, these data were recorded in the form of $N_{shell}(n,r)$. The Extreme Learning Machine(ELM)[15] was introduced to learn the mathematical relationship between electron density $N_{shell}(n,r)$ and the array (n,r). The meanings of these quantities have been explained in eq. 7 of main article. DFT calculation results were used as raw data of machine learning. After learning process, free electron density profiles of closed shell NaNPs containing more than 833 free s-band electrons can be predicted by ELM. The codes of ELM used in this project is "Extreme Learning Machine" in Python, based on scikit-learn.

Geometry in Core-shell model

The geometry size of NaNPs and AgNPs can be calculated by eq. 8 and eq. 9 in main article together with free electron density profiles in shell regions. The cut-off value of $\frac{N_{shell}(R_{shell})}{N_{core}}$ was set as 10%. Based on these assumptions, the radius of core and shell parts of MNPs with magic number of atoms can be calculated out, as is shown in Table S1 and S2. If more accurate simulations are to be conducted, the cut-off value can be reduced accordingly. In done so, the radius of shell parts of MNPs would be larger than the values listed in Table S1 and S2

Table S1. Geometry information of the size of the core vs. the shell of NaNP

Number of Na Atoms	Core (Å)	Shell (Å)
98	7.7	10.3
138	9.1	11.7
198	10.5	13.1
268	11.8	14.4
338	12.9	15.5
440	14.3	16.9
562	15.6	18.2
694	16.9	19.5

Table S2. Geometry information of the size of the core vs. the shell of AgNP

Number of Ag Atoms	Core (Å)	Shell (Å)
99	5.9	7.7
139	6.9	8.7
199	8.0	9.8
269	9.0	10.8
339	9.8	11.6
441	10.8	12.6
563	11.9	13.7
695	12.8	14.6

Field Enhancement at Central point of gap region

For NaNW dimers, the electric field enhancement in form of $|E^2/E_0^2|$ were calculated at the center point of gap regions, for both CTP/BDP mode and HCTP/BQP mode.

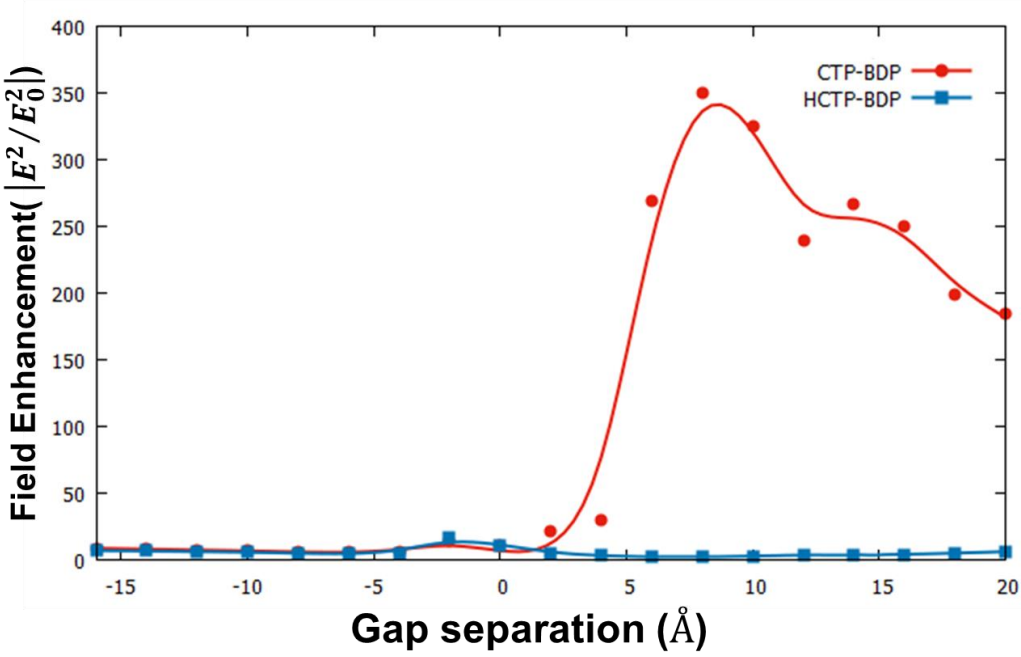

Figure S1. Electric field enhancement at the center point of gap regions of NaNW dimers under VEDP model.

Absorption Spectra of NaNP under multilayer shell VEDP

The absorption spectra of NaNP with 832 sodium atoms has been calculated under VEDP, with multi-shell layers in shell region of NaNP. As is shown in Figure S2. In multilayer approximation, the plasmon frequency of each layer remain unchanged, equals to value in the single layer shell, since plasmon frequency of materials depends on averaged value of free electron density over certain regions. The depths of shells are around 2 Å, and this is a sufficiently small value compared with incident wavelength. Making plasmon frequency an averaged value in such a thin layer helps to achieve good convergence in numerical simulations. For damping frequency, however, it increases dramatically in shell regions as the shell radius increases. Thus, taking this effect into account can improve the value of peak width at half height (PWHH) in spectra. In this project, damping frequencies of layers in shell regions are calculated based on eq. 3 in main article, and N_e was taken as the average value of free electron density in each layer. As shown in Figure S2,

the shape of absorption spectra tends to converge as number of layers in shell region increases to 6. All the damping frequencies used in multilayer shell VEDP from 2 layers to 6 layers are shown in Figure S3.

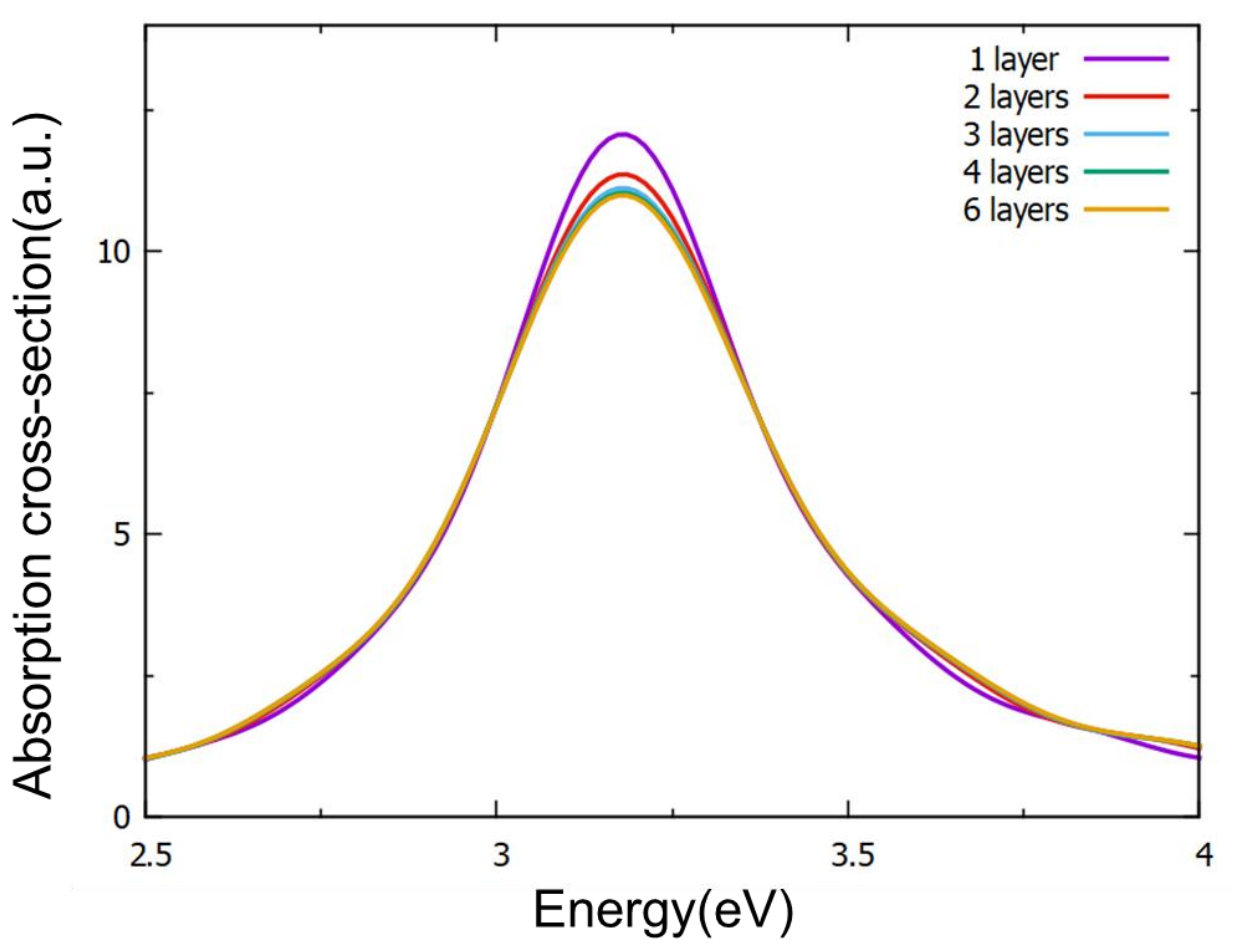

Figure S2. Absorption Spectra calculated under VEDP with 1 layer, 2 layers, 3 layers, 4 layers and 6 layers, respectively, in shell region of closed shell NaNP with 832 sodium atoms.

Table S3. Damping frequency (γ_p)of layers in multilayer shell VEDP of NaNP with 832 sodium atoms, values shown in unit of eV

NO. of layers	1st layer	2nd layer	3rd layer	4th layer	5th layer	6th layer
1	0.53					
2	0.39	0.81				
3	0.37	0.50	1.01			
4	0.36	0.43	0.62	1.15		
6	0.36	0.39	0.45	0.57	0.82	1.32

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