Supplemental Document

Journal of the Optical Society of America B
OPTICAL PHYSICS

Optical response and spill-out effects of metal nanostructures with arbitrary shape: supplement

HENG ZHANG AND CHUANFU HUANG*

School of Materials Science and Physics, China University of Mining and Technology, Xuzhou, Jiangsu 221116, China
**Corresponding author:* *chuanfuh@cumt.edu.cn*

Supplement DOI: https://doi.org/10.6084/m9.figshare.16635433

Parent Article DOI: https://doi.org/10.1364/JOSAB.431215

Optical response and spill-out effects of metal nanostructures with arbitrary shape

Heng Zhang and Chuanfu Huang*

School of Materials Science and Physics, China University of Mining and Technology, Xuzhou, Jiangsu 221116, China

A. The selection of electronic charge density formula

In the paper, we selected the electronic charge density in the jth layer as

$$n_j = n_j' = \left(1 - \frac{j}{N+1}\right) n_0 \tag{1}$$

Principally, the electronic charge density formula can also be expressed with other functional forms, e.g., we also tried to apply the following equation to get the sodium sphere and the sodium prolate spheroid resonance

$$n_j = n_j'' = \left(1 - \frac{2j-1}{2N}\right) n_0 \tag{2}$$

More specifically, the computation samples are computed with N=16, and the results are correspondingly shown in Fig. S1, where the sphere radius is 1.5 nm, and the spill-out thickness is exampled with 0.05 nm and 0.1 nm. Similar procedures are conducted for the prolate spheroid, with the long semi-axis of 1.5 nm and the short semi-axes of 1 nm.

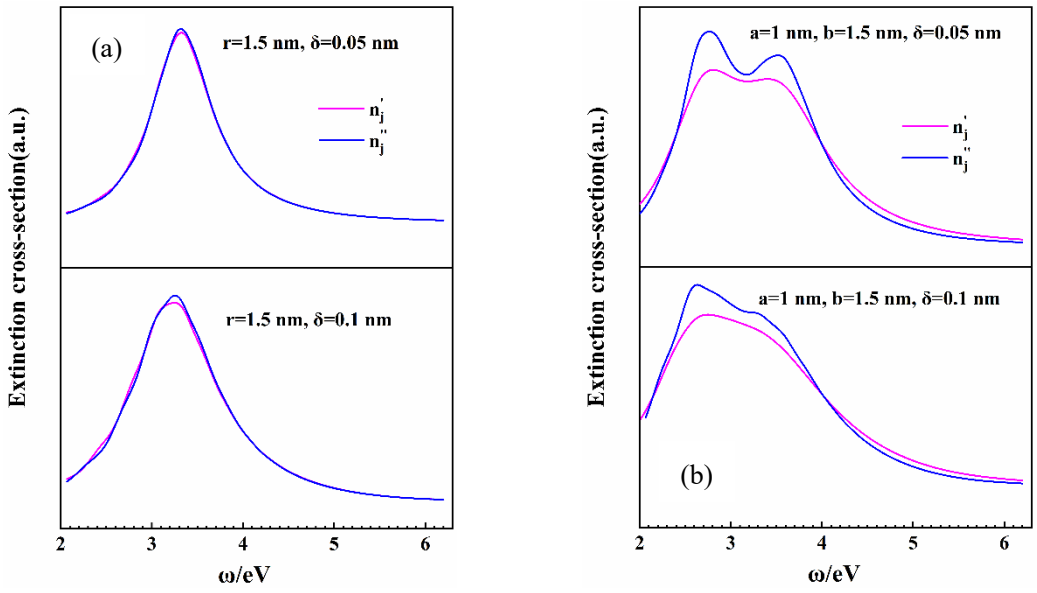

Fig. S1. With two different charge densities n_j' *and* n_j'', the optical responses of (a) the sodium sphere particle (r=1.5 nm) and (b) the sodium prolate spheroid particle (a=1 nm and b= 1.5 nm) are calculated for the spill-out thickness of 0.05 nm and 0.1 nm, with *N*=16.

From Fig. S1(a), it can be found that the resonance profiles calculated from n_j' and n_j'' are almost overlapped for the sphere particle, and this means that although the calculations are based on the

different functional form of electronic charges, the computed optical responses of the sodium sphere particle are close. In other aspects, Fig. S1(b) indicates the resonance profiles of the prolate spheroid are slightly different, but the overall trend of the profiles is still similar. Based on our understanding, the electronic charge density varying region can always be divided into N layers, as shown in Fig. 1 in the paper. If we compare Eq. (1) and Eq. (2) in this supplementary document carefully, it can be found that the electronic charge density of the $(j+1)$th layer will be increased by $-\frac{1}{N+1}n_0$ relative to that of the jth layer the with Eq. (1), while with Eq. (2), the increment will be altered to $-\frac{1}{N}n_0$ between the neighboring layer. As we know, the plasmonic properties are dependent on the electronic charge density, so these two equations can cause the jth layer electronic charge density are slightly dissimilar. However, if we can choose the total layer number *N* large enough, the optical response difference due to the charge density selection will be reduced. In other words, if *N* is sufficiently great, we should attain a unique and accurate response profile of the metal nanostructure. For instance, in this paper, *N* is assigned as 16, which is already closed to the ultimate resonance profiles, as indicated in Fig. S1. Based on the above discussion, we choose Eq. (1) as the electronic charge density for demonstrating the proposed model of the paper.

B. Multipeak analysis

In the paper, we applied the Lorentzian fit to the extinction curves with multiple peaks. Taking Figs. 2(a) and 2(c) as examples, it is not clear if these peaks are all dipolar in nature or we have other excitation patterns. If multipolar modes are existed, it will be incorrect to approximate the entire energy range with a single Lorentzian fit. After the following analysis, it can be found that the other multipolar modes do not require to consider in our research. Based on the MATLAB code written by Rasskazov,[1] which can calculate arbitrary multilayer spherical scattering fields, to calculate the precise optical response of spherical particles with considering the linear spill out of electrons, the peak analysis was conducted in this part. The Rasskazov's method is similar as the approach in our paper, which is to simulate and calculate the continuous spill out effect through the multilayers. The difference is that the finite element method of the COMSOL software in our paper can only calculate the case where the spill out layer is small. The MATLAB code of Rasskazov can calculate any layer to simulate the actual continuous spill out effect, but it can only be used for spherical particles. The peak analysis outcomes are summarized as follows:

1. For the sodium nanoparticle with radius r=3 nm, and delta=0.05 nm, the two cases of the dipole mode (l=1, 16 layers) and higher polar mode (l=6, the calculation order to 6, and 16 layers) are calculated with the MATLAB code. As shown in the attached Fig. S2, these two results named MATLAB l=1 and MATLAB l=6 are the *same* (looks like one curve) with the outcome of 16 layers computed in our manuscript. This coincidence proves that only the dipolar mode is dominant in the computation of our manuscript, and the multi-peak may be caused by the boundary between the layers when there is fewer spill out layers.

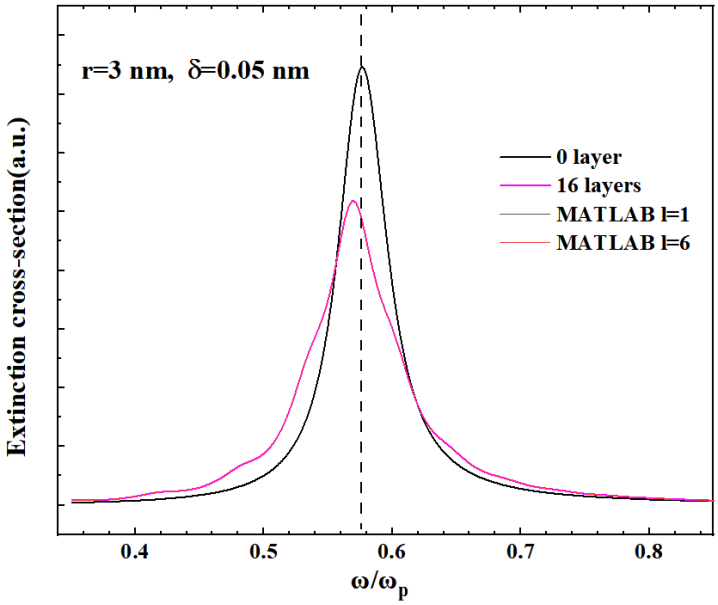

Fig. S2. For the sodium sphere with r=3 nm, and spill-out thickness δ=0.05 nm, the plasmonic behavior computed based on the 16 layer of the spill-out region in our paper is compared with the results from Rasskazov *et al*.

2. Next, for the sodium nanoparticle with radius r=3 nm, and delta=0.05 nm, but the spill out layers is taken to 100 layers. Similarly, the two cases of the dipole mode (l=1, 100 layers) and multipolar mode (l=6, the calculation order to 6, and 100 layers) are calculated with the MATLAB code. These two results are compared with the l6-layer Lorentzian fit in COMSOL, and it can be seen that the fitting result is in good agreement with the results of continuous spill out (MATLAB l=1 100 layers and MATLAB l=6 100 layers), as shown in Fig. S3. This means that the fitting in the manuscript can attain the satisfied results.

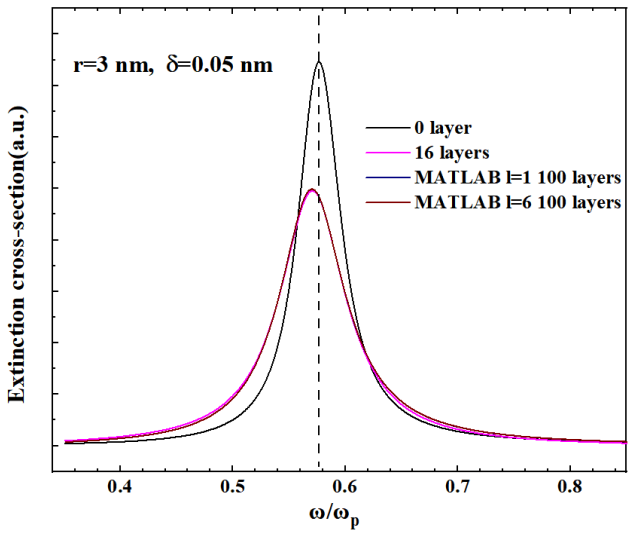

Fig. S3. For sodium sphere with r=3 nm, and spill-out thickness δ=0.05 nm, the plasmonic curve calculated based on the 16-layer fit in our paper is compared with the results from Rasskazov *et al*.

Thus, it is demonstrated that the multipolar modes did not exist in our calculation, so we do not

require to resolve the peaks to a specific mode.

References:

1. Ilia L. Rasskazov, P. Scott Carney, and Alexander Moroz, "STRATIFY: a comprehensive and versatile MATLAB code for a multilayered sphere," OSA Continuum 3, 2290-2306 (2020) https://doi.org/10.1364/OSAC.399979