Discrete dipole simulations of electron energy-loss spectroscopy and cathodoluminescence for particles near substrate

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The presence of a substrate under a particle significantly affects the electron energy-loss (EELS) and cathodoluminescence (CL) spectra. We extended the discrete dipole approximation to account for a semi-infinite substrate in EELS/CL simulations, this new capability is implemented into the open-source software ADDA. We use ADDA to numerically investigate how the spectrum changes depending on the thickness of a substrate under a silver nanodisc, starting from the nanodisc located in vacuum, then ranging the substrate thickness from 10 nm to 50 nm, and finishing with a semi-infinite substrate.

INTRODUCTION

Electron energy-loss spectroscopy (EELS) and cathodoluminescence (CL) are widely used to study the optical properties of nanoobjects. In the experiment, the sample is irradiated with relativistic electrons with an energy of about 100 keV. After the interaction with the sample, electrons' energies are measured and the energy-loss spectrum (EELS spectrum) is obtained. Simultaneously, the sample itself emits photons; this light is collected by a parabolic mirror to obtain CL spectrum. The main advantage of EELS/CL over optical methods is the ability to study optical properties with a spatial resolution of less than 1 nm (at wavelengths of visible light or even larger ones) [1]. To interpret the results of an experiment, a theory of fast-electrons interaction with an arbitrarily shaped sample is needed, as well as an appropriate computer simulation method.

We extend the capabilities of the discrete dipole approximation (DDA) to simulate EELS/CL, and realize it into the open-source software ADDA [2]. Until recently, there was only a theory for simulating the case of particles located in vacuum [3,4], which is never true in experiments, since the particle is always placed inside or on top of a substrate. We developed a theory for particles fully embedded into arbitrary (even absorbing) host medium [5], and showed that simulations in this approximation match the experiments where particles are placed inside slabs.

We further extended the theory to particles on top of a semi-infinite substrate and implemented it in ADDA. In the case of substrate, one needs to compute the incident field of an electron, which can be challenging. Thus, for calculating the incident field we use the image approximation. But the interaction of the particle with the substrate is calculated fully rigor-
ously, including calculation of Sommerfeld integrals, based on existing ADDA functionality [6].

In this work we consider these approximations for a silver nanodisc (50 nm diameter, 10 nm thickness) placed on top of Si$_3$N$_4$ substrate.

RESULTS

We simulated a silver nanodisc as a cylinder with a computational grid of 32x32x6 dipoles. Optical data for silver is taken from [7]; the refractive index of silicon nitride is considered to be constant and was set to 2 in all simulations. The electron with 100 keV energy was moving perpendicular to the surface of the plate 25 nm from its center, tangent to the side surface (Fig. 1a).

![Fig. 1. a) Illustration of the problem parameters. b) Dipole set visualization of the discretized nanoplate on top of a 30x100 nm substrate](image)

In Fig. 2 we compare the EELS and CL spectra obtained for different representations of the substrate. In the spectrum for the nanoplate in vacuum (Fig. 2, A), we observe a large peak at 2.7 eV, which redshifts in the presence of a substrate. For the cases B-H we simulate the substrate as a finite chunk of medium under the particle, which utilizes additional computational resources. For the I case we simulate the presence of a semi-infinite substrate (surface mode in ADDA), which does not require discretization of anything except the particle itself (as in vacuum), hence is much faster to compute (almost as fast as the case A).

The spectra for the cases B, C show that taking the substrate with the same thickness as the particle is not sufficient for approximating it with the semi-infinite approach, since the difference in the peak positions is at least 0.1 eV. The spectra for D-H show that the substrate of 20-30 nm thickness matches the semi-infinite case in terms of the peak position. The latter means that substrates that are 2-3 times thicker than the sample may be considered as semi-infinite.
infinite, and, therefore, simulated with much less computational resources needed. Note, however, that this case leads to large overestimation of absolute values of EELS probabilities, although they are rarely used in practice.

Fig. 2. EELS and CL spectra for nanoplate (see Fig. 1a for the problem parameters) with different representations of a Si₃N₄ substrate. A) In vacuum. B-H) On top of a finite-sized substrate (see the size in the legend, thickness×width. I) On top of a semi-infinite substrate.
In this work we numerically investigated how the thickness of a substrate under the particle affects the EELS/CL spectra. We showed that substrates that are 2 or more times thicker than the particle may be approximated as semi-infinite (with respect to peak positions), thus allowing much less computational resources needed for simulations.

The code used in this work is under development, but is available to a wide public at a separate fork https://github.com/alkichigin/adda/tree/sub, and can be already used for testing the substrate effects in EELS/CL simulations.

REFERENCES