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Discrete dipole approximation for low-energy photoelectron emission from NaCl nanoparticles

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ABSTRACT

This work presents a model for the photoemission of electrons from sodium chloride nanoparticles 50–500 nm in size, illuminated by vacuum ultraviolet light with energy ranging from 9.4 to 10.9 eV. The discrete dipole approximation is used to calculate the electromagnetic field inside the particles, from which the two-dimensional angular distribution of emitted electrons is simulated. The emission is found to favor the particle's geometrically illuminated side, and this asymmetry is compared to previous measurements performed at the Lawrence Berkeley National Laboratory. By modeling the nanoparticles as spheres, the Berkeley group is able to semi-quantitatively account for the observed asymmetry. Here however, the particles are modeled as cubes, which are closer to their actual shape, and the interaction of an emitted electron with the particle surface is also considered. The end result shows that the modeled emission asymmetry for these low-energy electrons is more sensitive to the interaction with the particle-surface than to the specific particle shape, i.e., a sphere or cube.

1. Introduction

The interaction of ionizing radiation with nanoparticles is important to understanding a variety of phenomena ranging from atmospheric nucleation to the heating of dust clouds by secondary electron emission from interstellar grains [1,2]. Photoelectron emission (PE) is currently being used as an analytical probe of soot formation within flames [3,4], for the detection of diesel emission [5], as spectroscopic probes of micron-sized droplet surfaces [6], sub-nanometer particles, and bio-aerosols [7]. A number of fundamental studies of nanoparticles, 5–200 nm in size, have revealed both unexpectedly large PE quantum yields [8] and circular dichroism [9], the magnitude of which depends upon particle size. In many of these studies, the role that particle size and shape plays in both the electromagnetic absorption and PE remains an active area of research.

In a recent publication [10], Wilson et al. measure the two-dimensional angular distributions of photoelectrons emitted from sodium chloride (NaCl) nanoparticles exposed to vacuum ultraviolet (VUV) light at various photon energies around 10 eV. The key finding is an asymmetry in the angular PE distribution. At photon energies where the electromagnetic absorption length in the NaCl material is on the order of, the nanoparticle size, emission is observed preferentially from the geometrically illuminated side of the particle relative to the shaded side. Moreover, this asymmetry is inversely proportional to the particle size.

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To investigate the cause and possible utility of this asymmetry, Wilson et al. employ a model of the emission process in which the particles are approximated as spheres and the PE trajectory within the particle is treated ballistically. Approximating the particles as spheres allows Mie theory to be used to calculate the internal (VUV) field from which emission is initiated. This model is able to reproduce the general trend of the observed PE asymmetry, implying that the asymmetry is due to the nonuniform illumination of the particle's interior caused by electromagnetic absorption. However, the agreement between the measured and modeled asymmetry is loose enough to suggest that a more sophisticated treatment could better fit the measurements. The following will describe such a model and compare its results to those reported by Wilson et al. More broadly, the following work demonstrates the application of a versatile electromagnetic-scattering model to a unique problem in nanoparticle science.

2. Model description

In the measurements [10], VUV light produced by the Advanced Light Source synchrotron at the Lawrence Berkeley National Laboratory is used to illuminate a stream of size-selected NaCl nanoparticles. The range of photon energies used include 9.4, 10.0, and 10.9 eV, which exceeds the NaCl ionization threshold [11] of 8.2 ± 0.1 eV, and the nanoparticle sizes range from approximately 50 to 500 nm. To acquire two-dimensional angular PE images, electrostatic lenses focus photoelectrons onto a dual multichannel-plate coupled to a phosphor screen, imaged onto a charged coupled device (CCD) camera. The resulting digital image is then numerically analyzed to infer the emission asymmetry.

The new model developed here begins with a representation of the nanoparticle shape. Fig. 1(a) shows scanning electron microscope (SEM) images of the types of nanoparticles used in the measurements. These particles are cube-like with rounded edges and some sign of either surface roughness and/or internal inhomogeneity. As an approximation, a homogeneous cube of length L is taken to represent a particle, see Fig. 1(b). Spherical model-particles will also be used to understand the effect of particle morphology on the PE emission. In the measurements, each particle enters the VUV beam in a random orientation, which is described in the model using two coordinate systems called the laboratory and particle-systems, (x_L,y_L,z_L) and (x_P,y_P,z_P), respectively. These systems share a common origin at the particle center, and the z-axis of the laboratory system is taken along the propagation direction of the VUV beam.

The electric field of the VUV light, which will be called the incident field $\boldsymbol{E}^{\mathrm{inc}}$, is taken to be a linearly polarized plane wave

$$\boldsymbol{E}^{\mathrm{inc}}(\mathbf{r}) = E_0 \exp(ik\hat{\mathbf{n}}^{\mathrm{inc}} \cdot \mathbf{r}), \tag{1}$$

where $\hat{\mathbf{n}}^{\mathrm{inc}}$ describes the propagation direction, and E_0 is a constant proportional to the light intensity. Meanwhile, the x_L and y_L-axes are taken along the particle-beam direction, and the direction from the origin to the detector, respectively, refer to Fig. 1(b).

The relative orientation of the two coordinate systems is described by the Euler rotation angles (α,β,γ); transformation between the systems is accomplished by a rotation matrix and its inverse [12]. A random particle-orientation can be realized by choosing three random numbers $\{x_1,x_2,x_3\}$ in the interval [0,1] from which the Euler angles are calculated as

$$\alpha = 2\pi x_1, \quad \beta = \cos^{-1}(2x_2 - 1), \quad \gamma = 2\pi x_3. \tag{2}$$

Defining N_{ori} sets of Euler angles this way results in a collection of as many particle orientations sampled randomly from all directions [13]. The number of orientations used in each simulation below is determined by observing the convergence of the asymmetry parameter (Section 3) with varying N_{ori}; in most cases a total of ten orientations is sufficient.

Next, the electric field $\boldsymbol{E}^{\mathrm{int}}$ inside the particle is found for each orientation. This is done using the Discrete Dipole Approximation (DDA), which in essence is a numerically exact way to solve the Maxwell equations for any particle [14]. To implement the DDA however, requires knowledge of the nanoparticle refractive index m, which is estimated [15] to be $m = 1.79 + 0.55i$ for a photon energy of 9.4 eV,

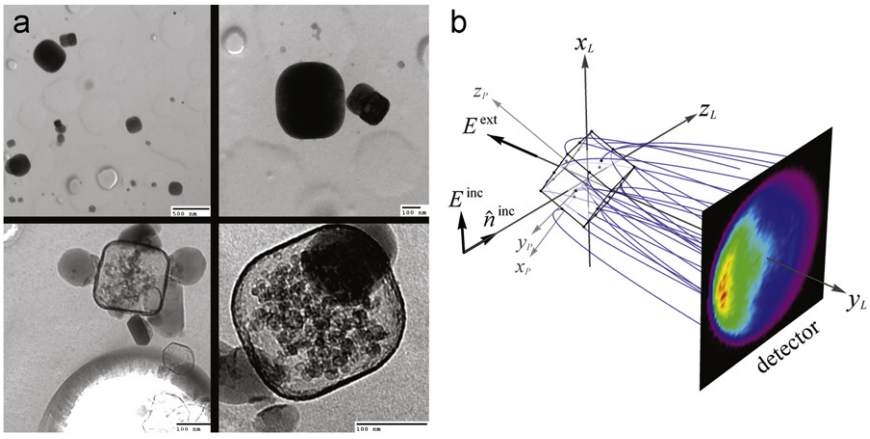

Fig. 1. SEM images (a) of the NaCl nanoparticles used by Wilson et al., and a diagram (b) of the modeled emission process.