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Progress Highlight

Probing local electromagnetic field enhancements on the surface of plasmonic nanoparticles

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ABSTRACT

Noble metal nanoparticles have attracted significant research interest due to their ability to support localized surface plasmons. Plasmons not only give the nanoparticles a characteristic color, but they also enhance electromagnetic fields at the nanoparticle surface, often by many orders of magnitude. The enhanced electromagnetic fields are the basis for a host of surface-enhanced spectroscopies, such as surface-enhanced Raman scattering (SERS), but characterizing how the enhanced electromagnetic fields are distributed on the surface of the nanoparticles is an experimental challenge due to the small size of the nanoparticles (~20–200 nm) relative to the diffraction limit of light. This Progress Highlight will discuss methods for characterizing local electromagnetic field enhancements with < 5 nm resolution, including electron energy loss spectroscopy, cathodoluminescence, and super-resolution optical imaging.

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1. Introduction

In 1857, Michael Faraday was the first to report on the remarkable ability of gold nanoparticles to produce diverse colors upon interaction with light; from these initial observations, the field of nanoplasmonics was born [1]. Today, we understand that noble metal nanoparticles, such as gold and silver, are able to support localized surface plasmons, which are collective oscillations of the surface conduction electrons produced by resonant electromagnetic (EM) excitation [2]. Faraday noted that the size of the nanoparticle should be smaller than the wavelength of the excitation light; this allows the electrons to move in concert in response to the incident field. The result is a "trapped" (rather than propagating) electron density wave, highly localized at the nanoparticle surface. Materials that support localized surface plasmons must have a negative real and small positive imaginary dielectric constant; in the visible region of light, these dielectric conditions are met by several noble metals, although gold and silver are most common due to their chemical inertness [2].

The excitation of a localized surface plasmon in a nanoparticle sample has two important implications: first, the nanoparticles will be strongly colored, with their extinction spectrum dependent on the nanoparticle shape, size, internal dielectric, and external environment (consistent with the observations of Faraday) [2,3]. Second, excitation of localized surface plasmons produce enhanced EM fields at the nanoparticle surface, which can be several orders of magnitude stronger than the incident EM field [4–6]. These enhanced EM fields have important implications for surface-enhanced spectroscopies, such as surface-enhanced Raman scattering (SERS) [7–9] and surface-enhanced fluorescence (SEF) [10,11], but also have demonstrated utility in photonic devices, such as plasmon-enhanced photovoltaic cells [12] and optical waveguides [13]. The extent to which the EM field is enhanced depends strongly on the shape and size of the nanoparticle, as well as the wavelength of the incident excitation. For example, a spherical nanoparticle illuminated by linear polarized light resonant with its dipolar plasmon mode has a predicted $|E_{loc,max}|^2/|E_{inc}|^2 \sim 400$ (where $E_{loc,max}$ is the maximum local EM field value and E_{inc} is the incident EM field) with the maximum field enhancement localized at the poles of the sphere [6]. On the other hand, multiple dipolar plasmon resonances can be excited in a dimer of spherical nanoparticles. When illuminated along the long axis of the dimer with resonant excitation, $|E_{loc,max}|^2/|E_{inc}|^2$ can exceed 10,000 due to the excitation of a coupled plasmon mode that leads to a strong EM field enhancement in the gap between the two spheres [6]. Lower wavelength light can also excite a second plasmon mode, oriented orthogonal to the dimer long axis, but with a lower overall EM field enhancement. Because of this strong shape and wavelength dependence, experimental methods that allow for improved understanding of how the enhanced EM fields are locally distributed on the surface of noble metal nanoparticles has been a longstanding goal within the plasmonics community.

This Progress Highlight will describe recent developments towards the characterization of plasmon-enhanced EM fields in noble metal nanoparticles with < 5 nm resolution. To date, a number of techniques have been applied to address plasmon-enhanced EM fields, including near-field scanning optical microscopy (NSOM) [14–21] and atomic force microscopy of light-driven morphological changes in nearby polymer films [22–24]. Although these scanning probe techniques provide extensive insight into how EM fields are locally enhanced on the surface of metal nanoparticles, they provide limited resolution due to the size of the scanning tip, often on the order of 20–50 nm. Photoemission electron microscopy has also been applied to the study of plasmonic nanoparticles, mapping the spatial origin of photoemitted electrons as a function of electromagnetic excitation, but also offers resolution on the order of roughly 20 nm [25–33]. This Highlight will describe several new methods that have emerged as complementary characterization tools for plasmonic nanoparticles in recent years: these include electron energy loss spectroscopy, cathodoluminescence, and super-resolution optical imaging. The application of these different techniques to measuring plasmon-enhanced EM fields will be described in the following sections, along with their associated advantages and disadvantages.