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Review

Near-field optical imaging of enhanced electric fields and plasmon waves in metal nanostructures

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ABSTRACT

In this article, studies on noble metal nanostructures using near-field optical microscopic imaging are reviewed. We show that near-field transmission imaging and near-field two-photon excitation imaging provide valuable methods for investigation of plasmon resonances in metal nanostructures. The eigenfunctions of plasmon modes in metal nanoparticles are directly visualized using these methods. For metal nanowire systems, wavevectors of the longitudinal plasmon modes can be estimated directly from the wave-function images, and the dispersion relations are plotted and analyzed. Using ultrafast transient near-field imaging, we show that the deformation of the plasmon wave function takes place after photoexcitation of a gold nanorod. Such methods of plasmon-wave imaging may provide a unique basic tool for designing plasmon-mode-based nano-optical devices. We also demonstrate that the near-field two-photon excitation probability images reflect localized electric-field enhancements in metal nanostructures. We apply this method to gold nanosphere assemblies and clearly visualize the local enhanced optical fields in the interstitial sites between particles (hot spots). We also show the contribution of hot spots to surface enhanced Raman scattering. The methodology described here may provide valuable basic information about the characteristic enhanced optical fields in metal nanostructures as well as on their applications to new innovative research areas beyond the conventional scope of materials.

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1. Introduction

Metal nanostructures show unique physical and chemical properties that are different than those of bulk materials [1–4]. For example, spherical gold and silver nanoparticles with diameters of several tens of nanometers show, respectively, characteristic red and yellow colors, which look very different from the bulk metals [1–4]. These colors are spectroscopically characterized by extinction peaks at ca. 530 nm for gold and around 400 nm for silver. In the field of chemistry, it has been known that gold clusters with diameters of a few nanometers or less show catalytic activity for various chemical reactions, while bulk gold is chemically inactive and very stable [5]. This example demonstrates that nanoparticles show very different chemical properties from bulk metals. The optical and spectroscopic characteristics of metal particles vary prominently in the range of several tens of nanometers in particle size [1–4], whereas chemical properties change drastically within a much smaller regime of a few nanometers or less. The characteristic optical properties of metal nanostructures arise from localized plasmon polaritons (hereafter called simply plasmons) [1–4,6], which are collective oscillations of conduction electrons coupled with electromagnetic waves. Extensive efforts have been made recently toward the construction of novel nano-optical systems [7–11] and the development of bio-chemical trace analysis sensors [12], based on the characteristics of plasmonic materials. Detailed analyses of optical and spectroscopic properties of metal nanostructures (particularly nanoparticles) and their origins are of fundamental importance not only for the basics of nano-optics but also for their application to the wide research fields of physics, chemistry, and biology.

The wave function of a plasmon resonance is a crucial feature of the nanostructure that governs its optical characteristics. Plasmon wave functions vary on the nanometric spatial scale. The optical characteristics of metal nanostructures consequently depend strongly on the geometrical structures in the nanometer regime. Strongly localized optical electric fields are sometimes generated in the vicinity of metal nanostructures [3,4,6,13–15]. Clarifying the optical properties with nanometer spatial resolution is hence essential for understanding and controlling the chemical and physical properties of metal nanostructures. This information is not only useful for plasmon studies, but also for optical measurements (such as absorption, emission, or scattering) in high spatial resolution, which in general give unique information on the molecular and electronic structures and excited-state dynamics of nanomaterials. Optical measurements with nanometric spatial resolution are thus highly desired.