A method to correlate optical properties and structures of metallic nanoparticles

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ABSTRACT

The optical response of individual nanoparticles is strongly influenced by their structures. In this report, we present a quick and simple pattern-matching based approach in which optical images of nanoparticles from localized surface plasmon resonance and single-molecule surface-enhanced Raman spectroscopy were used in conjunction with transmission electron microscopy for correlation of optical responses and the nanostructures of exactly the same nanoparticles or clusters of nanoparticles.

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1. Introduction

Metallic nanoparticles such as silver and gold have been the subject of intense research during the past decade due to their optical properties and tremendous potential in bio/chemical sensing [1–3], surface-enhanced Raman spectroscopy [4–7] and other surface-enhanced spectroscopies [8–10]. In order to tailor their unique properties and design functional materials and devices, a deeper understanding of the structure–property relationship of metal nanoparticles is required. In general, most previous studies on optical responses have been performed on a group of nanoparticles or a solution, leading only to the determination of the average optical properties of nanoparticles of various sizes and shapes. Only a very few direct experimental investigations of the morphological features of individual nanoparticle or clusters and the corresponding optical responses such as resonant frequency, resonant intensity and field enhancement have been reported [11,12].

Earlier efforts by other investigators to correlate the structures of individual nanoparticles with their optical responses have been modestly successful. For instance, *in situ* imaging and optical characterization using atomic force microscopy (AFM) [13,14] and scanning electron microscopy (SEM) [15] have been reported. However, these methods offer only limited spatial resolution. Transmission electron microscopy (TEM) is a powerful technique for such studies due to its much better spatial resolution than AFM and SEM and its unique capability of probing the internal structure of individual nanoparticles. However, difficulties in sample preparation and the lack of a quick and convenient method to locate the optically characterized nanoparticles in a TEM have thus far severely restricted the use of TEM for such comparative analyses.

In order to locate the optically characterized nanoparticles in a TEM, Jin et al. [16,17] presented a method in which Si_3N_4 substrates on TEM grids were marked using e-beam lithography thus enabling TEM imaging of the same nanoparticles. However, in addition to occasional spurious light scattering from the markers, the procedure is rather tedious. More recently, Novo et al. [18] used focused ion beam to mark references on the grid and use these as a guide in identifying the region of interest in a TEM. A much more efficient method was introduced by Mock et al.

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[19] in which they use pattern matching of wide-field optical imaging along with TEM imaging for a quick correlation of the optical spectral responses with the size and shape of individual silver nanoparticles.

In this report, we describe a method similar to the one followed by Mock et al., but with an important extension to exploit a conventional Cu grid as a graph. We show examples of this method to study single-molecule surface-enhanced Raman spectroscopy (SMSERS) and localized surface plasmon resonance (LSPR) spectroscopy responses and their dependence on the structure of the individual or cluster of nanoparticles using TEM. This procedure enables quick and high-throughput investigations to correlate optical properties with the corresponding structures of nanoparticles.

2. Experimental methods

Colloidal suspensions of silver nanoparticles were synthesized by reducing silver nitrate with sodium citrate by an established scheme pioneered by Lee and Meisel [20].

Most of the nanoparticles in the suspensions synthesized using this method were spherical with diameter ~40 nm. Several other shapes such as triangular prisms, rods, cubes, hexagonal plates were also present. The detailed procedure of nanoparticles synthesis is described elsewhere [21].

The TEM grids used in this study were made of copper and 50-nm-thick formvar with a surface coating of 2–3-nm-thick amorphous carbon obtained from Ted Pella Inc. The structural integrity of the TEM grids with only formvar layer was found to be poor in comparison to those with the carbon layer and therefore they were not preferred.

A 2–10 μl nanoparticle suspension was dropped on the surface of the TEM grids. It was found to be important to let the solvent completely evaporate from the TEM grids before placing it on glass slides to avoid preferential segregation of the suspension onto the glass surface due to the hydrophilic nature of glass. The glass slide held the TEM grid above the (optical) microscope objective. The nanoparticles were on the top of the grid, away from the glass. The glass slide also helps protect the grid from contact with the oil immersion objective during optical characterization described later. The samples were then held in an N_2 environment for ~1 h, then immediately subjected to optical characterization to prevent potential contamination due to exposure to air.

In cases where the nanoparticles were not well dispersed on the TEM grid, ambiguities may arise during identification of the nanoparticle in TEM. This problem was overcome by carefully controlling the concentration of silver nanoparticles in the solution. Since the final density of the particles also depends on how the solution was placed and dried on the grid, several attempts were sometimes required to ensure that the particles were well separated, but not too sparse to establish a useful pattern.

In order to index the regions of interest to facilitate locating them again in a TEM, the distinctive center of the grid, indicated by an asterisk mark in Fig. 1(A), was used as a reference and the coordinates were determined for each section of the grid. As shown in Fig. 1(A), the grid was divided into four quadrants: (+,+), (+,−), (−,+), (−,−), analogous to a simple graphing methodology. The numbers and the signs provide the coordinates of the region of interest. A lower resolution optical image containing approximately all the particles in a specific section of the grid was recorded, as shown by Fig. 1(C), which was then used to
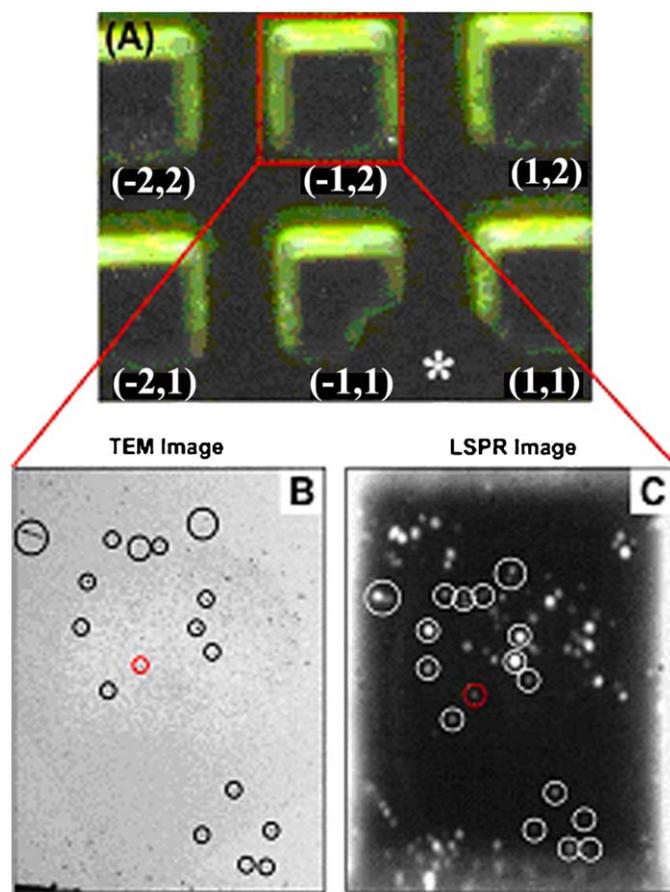
Fig. 1. Correlation of TEM and LSPR images. (A) Low resolution (40×) dark-field image of grid (−1,2). Note the distinctive center of the grid in the bottom row, indicated by an asterisk (*), that can be used as the origin in determining the coordinates, (B) TEM image of grid (−1,2) and (C) LSPR image (100×) of grid (−1,2).
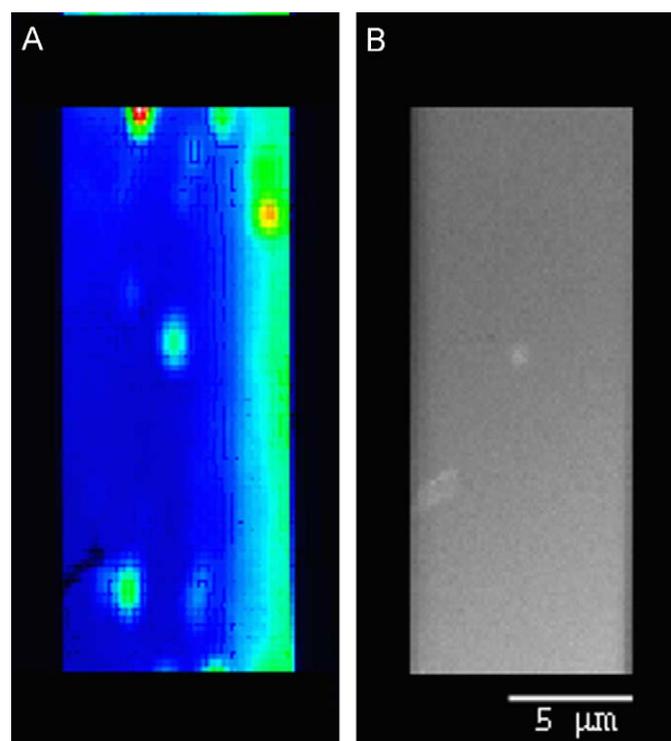
Fig. 2. (A) LSPR image and (B) SMSERS image of the same region on the TEM grid.
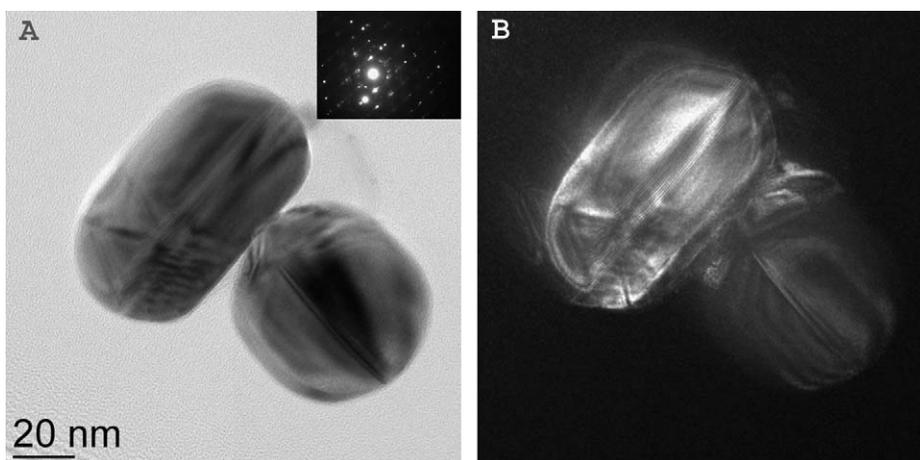
Fig. 3. (A) Bright-field with diffraction pattern inset and (B) dark-field TEM image of the SMSERS active nanoparticle identified based on pattern matching using LSPR, SMSERS and low-magnification TEM imaging.

compare and map in TEM to locate the nanoparticles based on pattern recognition of a local region.

In this study, all optical response spectra from single nanoparticles scattering were obtained with either a Nikon Eclipse TE300 or Nikon Eclipse TE2000-U inverted optical microscope (Nikon, Japan) coupled to a SpectroPro 300i imaging spectrometer and a liquid nitrogen cooled Spec-10:400B CCD detector. Both microscopes have tungsten filament illumination sources. The illumination was focused on the sample surface by a Nikon 0.8–0.95 numerical aperture (NA) dark-field condenser. The light scattered by the nanoparticles was detected by the collection optics. It is critical that the NA of the objective (collection optic) is smaller than the NA of the condenser to avoid collection of illumination light signals. Therefore, a Nikon variable aperture (NA = 0.5–1.3) 100 × oil immersion objective was chosen.

Following the optical spectroscopic investigations, the samples were transferred to a JEOL JEM-2100F Fast TEM (Tokyo, Japan) operating at 200 kV to acquire standard bright-field/dark-field images and diffraction patterns of the nanostructures.

3. Results and discussion

The SMSERS active nanoparticles were identified by acquiring an SMSERS image and comparing it with the LSPR image of the same region. These two images were then used during TEM imaging of the same grid to positively identify the SMSERS active nanoparticle aggregates.

It should be noted that, because of the strong plasmon resonance effects in silver nanoparticles, they were easily detectable in optical CCD images, despite the fact that their sizes (less than 100 nm) were well below the detection limit of an optical microscope. However, the nanoparticles were much difficult to detect in a TEM at lower magnifications because of their relatively weak interaction with the electron beam. Therefore, careful alignment of the sample grid orientation in TEM to that used during optical measurements was required to improve the contrast and thereby, the efficiency of pattern matching. Severely underfocusing the sample with respect to the electron beam also improved the contrast and hence facilitated pattern matching at low magnifications.

Fig. 2 shows the LSPR and SMSERS images of the same region on the grid. Note that only a small fraction of the nanoparticles display SMSERS activity. The SMSERS active region was then identified in the TEM based on the pattern-matching-based approach described earlier, and the corresponding bright- and

dark-field images and the diffraction pattern were obtained as shown in Fig. 3 below, allowing complete crystallographic characterization. With this high-throughput methodology to determine the structure of SMSERS active nanoparticle aggregates, the relationship between the optical responses and the nanostructures can be systematically studied.

4. Summary

In this report we have presented a convenient, high-throughput methodology based on pattern matching of LSPR and SMSERS images with TEM images to determine the structural information of SMSERS active nanoparticles. This procedure offers a highly efficient and quick method to correlate the nanostructure with the optical responses of nanomaterials. Further details and results from the optical analyses pertaining to the SMSERS enhancement and single-molecule sensitivity are presented elsewhere [22] and compared with theoretical electrodynamics calculations.

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