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Studying substrate effects on localized surface plasmons in an individual silver nanoparticle using electron energy-loss spectroscopy

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ABSTRACT

In this study, electron energy-loss spectroscopy (EELS) in conjunction with scanning transmission electron microscopy (STEM) was used to investigate surface plasmons in a single silver nanoparticle (NP) on a magnesium oxide substrate, employing an incident electron trajectory parallel to the substrate surface. This parallel irradiation allowed a direct exploration of the substrate effects on localized surface plasmon (LSP) excitations as a function of the distance from the substrate. The presence of the substrate was found to lower the symmetry of the system, such that the resonance energies of LSPs were dependent on the polarization direction relative to the substrate surface. The resulting mode splitting could be detected by applying different electron trajectories, providing results similar to those previously obtained from optical studies using polarized light. However, the LSP maps obtained by STEM-EELS analysis show an asymmetric intensity distribution with the highest intensity at the top surface of the NP (that is, far from the substrate), a result that is not predicted by optical simulations. We show that modifications of the applied electric field by the substrate cause this asymmetric intensity distribution in the LSP maps. These results demonstrate some of the characteristic behavior inherent in EELS analyses of LSPs in metallic NPs on a dielectric substrate.

1. Introduction

The oscillating charges of localized surface plasmons (LSPs) in metallic nanoparticles (NPs) are accompanied by enhanced electromagnetic fields confined within regions smaller than the optical diffraction limit. LSPs in metallic NPs have found applications in biological sensing [1–3], fluorescence resonant energy transfer [4–6], solar light harvesting [7–9], photocatalysis [10,11], optical waveguides [12–14] and metamaterials [15–17]. Since the physical properties of LSPs are sensitive to the environment surrounding the NPs as well as to the NP structure, it is important to be able to investigate LSPs in individual NPs supported on substrates with high spatial resolution. The presence of a dielectric substrate beneath an NP produces a shift in the resonance energy of the NP, and also results in mode splitting due to reduced symmetry, effects that have been firstly observed for a single silver nanocube supported on a dielectric substrate using dark-field microspectroscopy [18]. This mode splitting corresponds to proximal and distal modes associated with a strong electromagnetic field either near to or far from the substrate, respectively [18,19]. Similar mode splitting due to the reduced symmetry has been found in a spherical NP supported on various substrates using polarized light experiment, showing the dipole plasmons oscillating parallel and perpendicular to the substrate [20]. High spatial resolution studies of LSPs have been performed using electron energy-loss spectroscopy (EELS) in conjunction with scanning transmission electron microscopy (STEM) [21–27], and have shown peak shifts due to particle size and substrate effects [28–31]. EELS observations of silver nanocubes on dielectric substrates have demonstrated that the shift of the proximal mode to a lower energy is a substrate effect.

In the present work, we generated EELS maps of a silver NP supported on a magnesium oxide (MgO) substrate. Spectrum-image (SI) data were acquired using an electron probe to irradiate the sample parallel to the interface between the NP and the substrate, allowing us to directly investigate substrate effects on LSP excitations as a function of the distance from the substrate. The geometric relationship of the irradiation to the specimen meant that a direct theoretical analysis could be performed, based on simulations of the electron trajectory using the discrete dipoles approximation (DDA) method. We found out that the EELS technique was able to discriminate between LSPs oscillating parallel and perpendicular to the substrate surface, providing the same results as are normally obtained from analysis using polarized light [20]. The spatial distribution intensity of the energy-loss probability of an LSP was found to be weak in the vicinity of the NP/substrate interface, while this same distribution was enhanced at the

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upper surface of the NP (that is, far from the substrate). It appears that this substrate effect is only observed in EELS data, and is attributed to the electric field generated by an incident electron and the associated image charge in the substrate.

2. Experimental

Experimental specimens were prepared by first collecting MgO NPs on a thin carbon film. These MgO NPs were subsequently coated with silver NPs by vapor deposition under a 200 Pa argon gas atmosphere. Since MgO has a wide band gap of 7.8 eV and a medium dielectric constant, it is suitable for the mapping of LSP excitations in silver NPs and also for studying the substrate effect. The STEM-EELS data were acquired using a spherical aberration-corrected instrument (JEM-9980TKP1) operating at an accelerating voltage of 200 kV. The incident electron probe, with a size of approximately 0.1 nm, was formed with a convergence semi-angle of 23.6 mrad. SI data were obtained with an energy resolution of 0.5 eV, a collection semi-angle of 10 mrad and a spatial sampling of 1 nm per pixel. The zero-loss tail was subtracted from each EEL spectrum by fitting the spectrum acquired in vacuum. The experimental data were interpreted by performing DDA simulations, in which the targets were described as aggregates of discrete dipoles, using the DDEELS code [32]. In these calculations, the dielectric functions of silver were those previously published by Palik [33], while the dielectric function of MgO was assumed to have a constant value of 3.13 [34]. The radius of each discrete dipole was set to 0.45 nm, and the presence of the dielectric substrate was taken into account by employing the image charge method, as discussed below.

3. Results and discussion

Fig. 1 shows the experimental results obtained from a silver nanosphere supported on an MgO substrate. The high-angle annular dark-field (HAADF) image in Fig. 1a demonstrates that the silver NP had an almost spherical shape with a radius of 8 nm. Fig. 1b presents the spectra extracted from top (indicated by A), side (B) and gap (C) regions around the NP, at a distance of 1 nm from the surface of the particle, as indicated in Fig. 1a. Fig. 1c shows the EELS map obtained over the energy window of 3.3 ± 0.3 eV demarcated by the dashed lines in Fig. 1b. The substrate effects are clearly observed in the EEL spectra and in the map, and appear as a slight peak shift in the spectra and as the asymmetrical intensity distribution in the map. The spectra extracted from the A and B regions exhibit LSP peaks at 3.4 and 3.5 eV, respectively, indicating that the peak energy of the B region spectrum was 0.1 eV higher than that of the A region. This peak shift can be attributed to a substrate effect because it is larger than would be expected based on the aspect ratio of the NP [35]. In the EELS map in Fig. 1c, the highest intensity is observed at the top area (region A) of the NP, while the intensity at the gap area (C) is very weak. Generally, it is expected that, upon the light excitation of an LSP in a metallic NP supported on a dielectric substrate, the strong electric field induced by the LSP will be confined to the gap between the NP and the substrate, representing a so-called hotspot [36]. It has been previously reported that EELS is blind to hotspots in the gaps between metallic NP dimers due to the symmetric structure [24,37–39]. However, the present case involves neither a symmetric structure nor a metallic dimer, and so the observed LSP intensity distribution is attributed to the substrate effect.

To understand the substrate effect observed in our data, we performed DDA simulations for a silver NP on an MgO substrate. Fig. 2a presents the EEL spectra calculated for three different electron trajectories, as shown in the model (inset), consisting of a silver nanosphere with a radius of 8 nm and an MgO substrate with a semi-infinite size. These results are compared with the spectrum calculated for an isolated silver NP in a vacuum, indicated by the black line. The LSP peaks of the NP on the substrate appear at slightly lower energy values than that of the isolated NP. This red shift of LSP peaks represents the substrate effect [40]. For the electron trajectory in region A, the LSP peak appears at 3.4 eV, which is 0.05 eV lower than that for trajectory B, a result that is in good agreement with the experimental data when the extra shift of 0.05 eV due to the aspect ratio of the NP is considered. This peak shift is related to the direction of polarization induced in the NP. The LSP dipole modes for which the polarization is perpendicular or parallel to the substrate are excited by electrons having trajectories A and B, respectively. Polarization perpendicular to the substrate localizes the charges near the substrate surface, resulting in a stronger interaction between the NP and the substrate compared to parallel polarization. Therefore, the resonance energy of the LSP with polarization perpendicular to the substrate is lower than that of the LSP having parallel polarization [20]. It should be emphasized that the EELS technique can evidently detect shifts in the LSP peak resulting from the variations in the polarization direction relative to the substrate, an effect that has previously been observed using polarized light. The intensity of the LSP peak associated with trajectory A is strong compared to that for an isolated NP, while that for trajectory C is considerably weaker. This characteristic intensity distribution is also noticeable in the LSP map shown in Fig. 2b, which was calculated from the intensity at 3.4 eV. The LSP excitation probability for the NP is enhanced at the top surface, far from the dielectric substrate, and is suppressed in the gap region, an effect that is closely reproduced in the experimental LSP map.

Next, it is helpful to discuss the asymmetric spatial distribution of the energy-loss probability, which is the substrate effect particular to

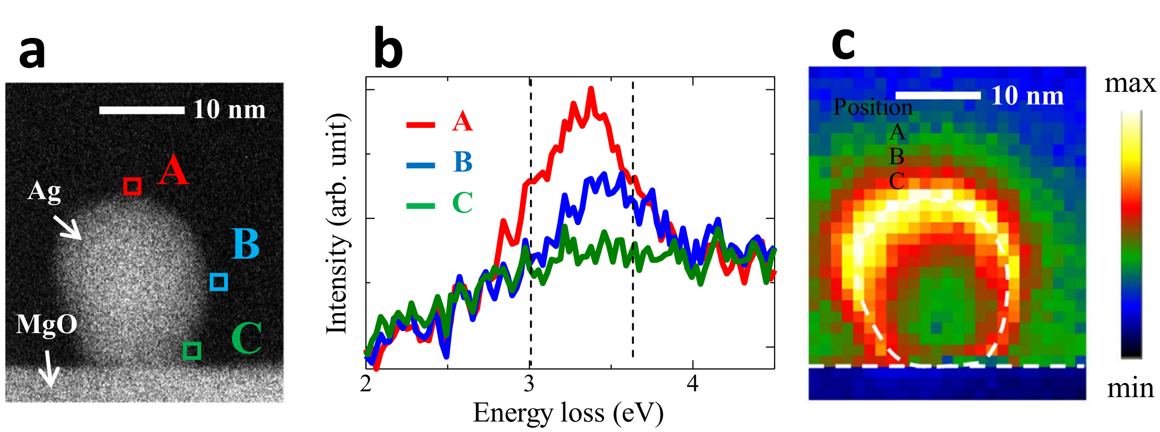

Fig. 1. Experimental EELS results obtained from a silver NP placed on a magnesium oxide substrate, applying electron irradiation in the direction of the cross-section. (a) HAADF image, in which three 2 nm squares are indicated, each 1 nm from the NP surface. (b) EELS spectra obtained from the top, side and gap regions indicated in (a) as A (red), B (blue) and C (green). (c) EELS map generated using an energy window from 3.0 to 3.6 eV, corresponding to the black dashed lines shown in (b). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)