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Plasmon Excitations in Bimetallic Ag Nanostructures by Monochromated E-beam

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Plasmonic nanomaterials have attained enormous research interest because of their characteristics for applications such as biological and chemical sensing, catalysis and energy harvesting. Recently, we have seen that bimetallic nanoparticles (NPs), consisting of immiscible Ag and Co, have ten folds better oxidation resistance in ambient environment and thus exhibit ultrastable plasmonic behavior [1]. In addition to that, it has been seen that the bimetallic Ag-Co NPs show large tunability in the wavelength of localized surface plasmon resonance (LSPR) with size and composition, and has comparable LSPR detection sensitivity to refractive index changes compared to pure Ag nanoparticles [2]. Such interesting results made Ag-Co bimetallic NP system as a suitable candidate to study surface plasmon excitations via electron beam at a very localized scale in a scanning transmission electron microscope (STEM) [3].

We study surface plasmon resonance (SPR) behavior in bimetallic Ag-Co and pure Ag NPs. For this investigation, imaging and low-loss EELS of the nanoparticles were performed in Zeiss Libra-200 equipped with monochromator and energy filter. The low-loss energy spectra were taken with a dispersion of 0.05eV per channel over an exposure time of 0.1 sec. The energy resolution of the collected spectra was 0.15eV. Low-loss EELS, in general, is affected by the influence of large tails of zero-loss peak, which suppress the features in the data such as surface plasmon etc. This problem is dealt by the introducing monochromated electron source in TEM which reduces the energy spread of the beam. The quantitative analysis of the data is critical towards understanding near field plasmonic behavior.

However, general literature does not discuss a highly quantitative description of SPs from EELS measurements and therefore, do not present the full capabilities of EELS measurement in STEM. In addition, the existing analysis techniques do not fully complement the high quality of EELS data that can be generated by latest state-of-art instruments. Here, we show a method to quantitatively analyze low-loss EELS data to maximize the extraction of plasmon related information. In order to quantify low-loss electron energy spectra, a new analytical method was adopted. In this method, first, zero-loss peak was modeled with an analytical function as shown in Fig. 1(a). As plasmons follow a Lorentzian profile, low loss spectrum (1-30 eV) was fitted with appropriate number of Lorentzians by using non-linear curve fitting method with the help of scipy numerical package. With this analysis technique, energy position, band width and scattering intensity of each surface plasmon is obtained. The fitted curve is shown in Fig. 1(b) where low-loss spectrum is taken from the encircled region of the NP shown in the inset. The average energy position of each excited plasmon on NP surface is tabulated in Table 1 which shows extremely small standard deviation and thus high reliability of the method. This study shows the detailed analysis of plasmonic response in an individual bimetallic nanoparticle with high special resolution; and thus provides a strong microscopy tool to understand the evolution of average plasmonic behavior of bimetallic Ag-Co nanoparticle arrays for bio-sensing devices.

References

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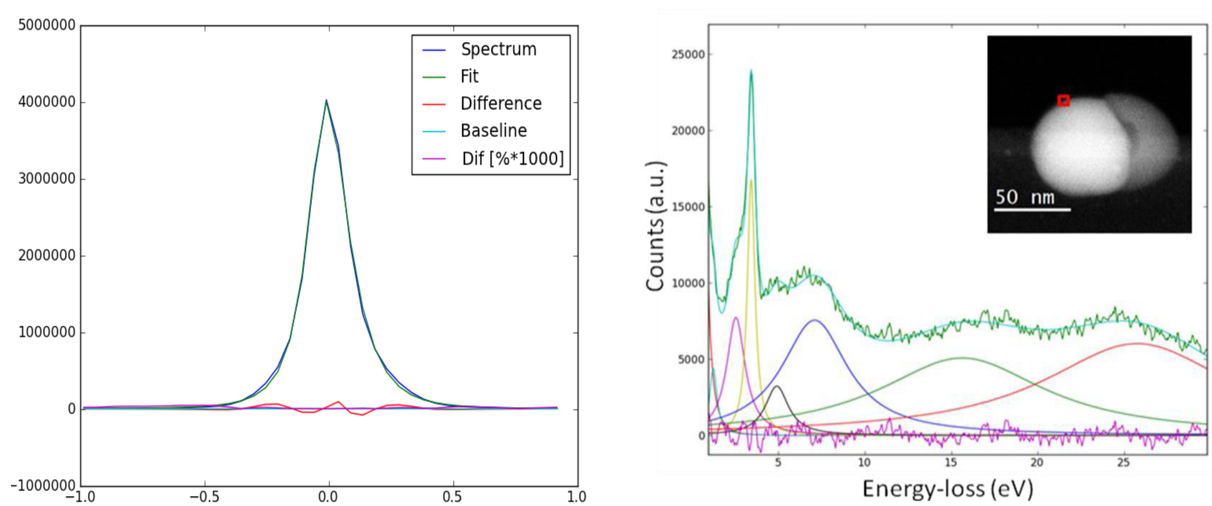

Figure 1. (a) A typical zero-loss EELS peak fitted with the zero-loss analytical function. (b) An EELS experimental spectrum along with the fit based on various Lozentzian peaks.

Bimetallic Ag-Co NP			
Ag region		Co Region	
E_{max}(eV)	ΔE_P(eV)	E_{max}(eV)	ΔE_P(eV)
2.50 ± 0.07	1.2 ± 0.1	2.60 ± 0.03	1.53 ± 0.07
3.42 ± 0.08	0.6 ± 0.04		
5.0 ± 0.1	2.0 ± 0.3	5.6 ± 0.1	3.1 ± 0.1
7.2 ± 0.3	4.3 ± 0.3	8.1 ± 0.2	5.4 ± 0.4

Table 1. Table showing excited plasmon energies in Ag and Co regions of Ag-Co NP.