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STEM-EELS Evaluation of the Dependence of Localized Surface Plasmon Linewidth on the Size of Au Nanoparticles

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Localized surface plasmon (LSP) excitations in metallic nanoparticles (NPs) have recently received increasing attention because of their potential applications in solar energy harvesting, photocatalysis, sensing and biology. Both the LSP resonance energy and peak linewidth depend on the size, shape and environment of the metallic NP, especially for NPs with sizes < 5 nm [1-2]. With smaller metal NPs quantum size effects, surface diffuse scattering and metal-support interactions can all affect their LSP resonant energies and linewidths. The improved energy resolution of the electron energy loss spectroscopy (EELS) in a monochromated STEM (STEM-EELS) makes it possible to study the intrinsic properties of LSPs in individual small metallic NPs [3]. We report here the STEM-EELS investigation of the dependence of LSP linewidths on the Au NPs in the size range of 4-20 nm in diameter.

The Au NPs were synthesized by reduction of $HAuCl_4$ in $NaBH_4$ solution and were then dispersed onto ultrathin silicon nitride (SiN_x) substrate. The STEM-EELS experiments were conducted on a Nion UltraSTEM^{TM} 100 equipped with a monochromator, a C3/C5 aberration corrector and a Gatan Enfina electron energy-loss spectrometer. The EELS spectra were acquired with a dispersion of 5 meV per pixel, a probe convergence semi-angle of 30 mrad and a collection semi-angle of 45 mrad, resulting in an energy resolution of ~15 meV in the acquired EELS spectra and significantly reducing the tailing effect of the zero-loss peak on the detection of low-energy loss peaks [4]. The experimental setup is shown in Fig. 1a. The aloof beam condition was used to excite the LSPs in Au NPs.

Figure 1b shows a HAADF image of an Au NP of interest and the corresponding EELS spectra acquired at the different positions were shown in Fig. 1c. The LSP resonant peak at ~ 2.34 eV is clearly revealed when the electron beam was at aloof positions. When the electron beam passed through the center of the Au NP a prominent broad peak at ~ 2.44 eV was observed, reflecting the excitation of Au bulk plasmons. All the three spectra in Fig. 1c show non-symmetric profiles, presumably caused by the overlap with the energy loss peak of the inter-band transitions of Au 5d electrons to the 6sp orbitals. Figure 2a displays a series of EELS spectra, obtained with an aloof beam, of Au NPs with sizes from ~23 nm to ~5 nm in diameter. The signal-to-noise ratio of the LSP resonant peak decreases with decreasing particle size but is still good enough for quantitative analysis. The linewidth of the Au LSP resonant peak increases significantly with decreasing particle size. Figure 2b plots the dependence of the full-width-at-half-maximum (FWHM) values of the Au LSP resonant peaks, estimated by fitting the left half of the experimental peak profiles to the corresponding Lorentzian shapes, on the diameter of the Au NPs. When the Au NP size changes from ~ 23 nm to ~ 5 nm the FWHM value of the LSP resonant peak changes from ~0.5 eV to ~1.4 eV. Figure 2c plots the FWHM value against the inverse of the particle diameter. We can conclude that for larger particles (> 5 nm), the broadening of the LSP resonant peaks can be considered to be linearly proportional to the inverse of the particle size. For much smaller Au NPs, the peak broadening, however, seems to increase more rapidly with the decreasing size of the Au

NPs. The peak broadening mechanisms and the effects of the metal-substrate interaction on the peak broadening are investigated [5].

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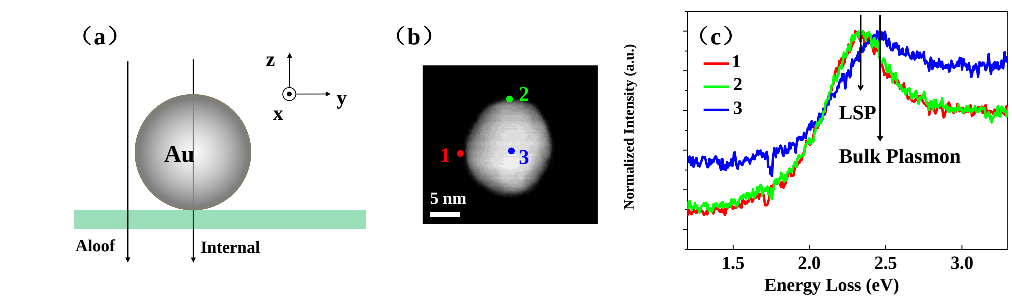

Figure 1. (a) Schematic of the experimental EELS setup; (b) HAADF image of an Au NP and (c) EELS spectra from the Au NP in (b) at different beam positions. Aloof (1, 2) and internal (3) beam condition. The EELS spectra were normalized at the peak intensity.

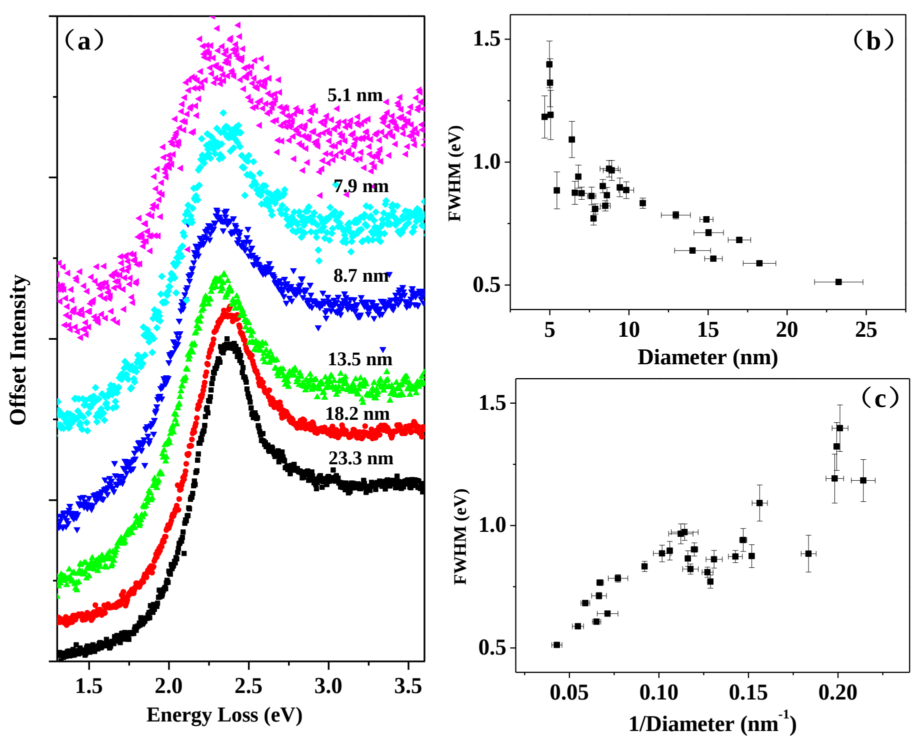

Figure 2. (a) A series of EELS spectra obtained from different sizes of Au NPs with aloof beam condition. (b) Plot of experimental FWHM values of LSP resonant peak *vs.* diameter of Au NP. (c) Plot of FWHM values of LSP resonant peak *vs.* 1/diameter for Au NPs of different sizes. The peak broadening becomes much more significant for smaller Au NPs.

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