

Optimizing Nanostructure Size to Yield High Raman Signal Enhancement by Electron Energy Loss Spectroscopy

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The Raman signal from an organic molecule can be significantly enhanced by its contact with a noble metal surface. This phenomenon, known as surface enhanced Raman spectroscopy (SERS) in biological and chemical sensing applications, is strongly related to the localized surface plasmon resonance (LSPR) of the nanostructures [1]. Here we use electron energy loss spectroscopy (EELS) to study the relationship between nanoparticle structure and LSPR, and the overall effect on Raman signal enhancement.

Nanodisc arrays of gold with diameters of 150nm, 90nm, 75nm and 55nm were fabricated directly on Si₃N₄ membrane TEM grids using electron beam lithography (Fig. 1) [2]. EELS spectrum images were collected around four discs in each array (inset of Fig. 2a) using a monochromated scanning transmission electron microscope (mono-STEM) operated at 300kV. For each individual nanodisc of 150nm in diameter, the EELS spectrum close to the edges (black) differs from that in the disc center (green). The EELS intensity map at electron energy loss of 1.7eV (Fig. 2b) shows that the strongest surface plasmon mode is located closely to the nanodisc edges. A dark mode, manifested as an additional peak at 2.3eV, resides primarily in the center of nanodiscs (Fig. 2c) [2].

Fig. 3a shows EEL spectra around edges of different size nanodiscs and the 638nm laser energy (1.9eV) used for the Raman excitation. In order of increasing LSPR energy, we found 1.7eV for 150 nm nanodiscs, 1.9eV for 90 nm nanodiscs, 2.0eV for 75 nm nanodiscs, and 2.1eV for 55 nm nanodiscs. This red shift of surface plasmon energy as nanodiscs size increases is also observed in various optical and simulation studies [3,4]. The same samples coated with Rhodamine 6G were subsequently illuminated with a 638nm laser to collect Raman spectra (Fig. 3b) using a Horiba XploRA+ confocal Raman microscope. We observed that when the excitation laser energy is very close to LSPR (as in the case of 90nm nanodisc array for which the mismatch is less than 5%), the Raman signal experiences a significant enhancement compared with off-resonance situations. This observation strongly supports an electromagnetic enhancement mechanism [2]. A damped harmonic oscillator model is implemented to estimate Raman intensity in Fig. 3c and shows reasonable agreement with experimentally measured values.

This study demonstrates that surface plasmon response can be finely tuned to match the excitation laser energy by controlling nanostructure size to achieve optimum Raman signal enhancement. It will serve as a useful tool to engineer nanoparticles for cancer diagnostics and treatment [5].

References:

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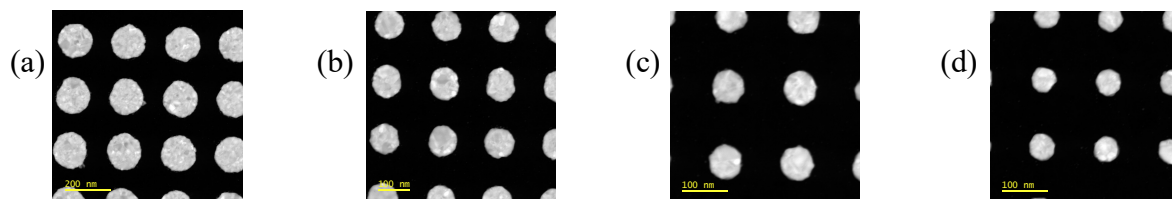


Figure 1. Annular dark field images of nanodisc arrays with the same edge to edge spacing of 90nm and diameters of (a) 150nm, (b) 90nm, (c) 75nm and (d) 55nm.

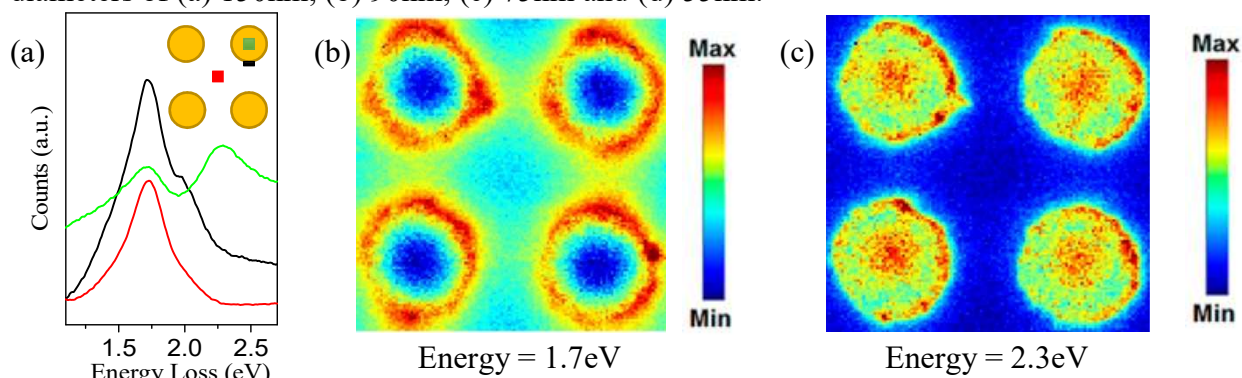


Figure 2. (a) EELS spectra from the 150nm diameter array at the red, black and green boxed regions. (b) EELS intensity map of 150nm disc array at energy loss of 1.7eV showing strongest surface plasmon modes located near edges and (c) at energy loss of 2.3eV showing dark modes in the disc centers [2].

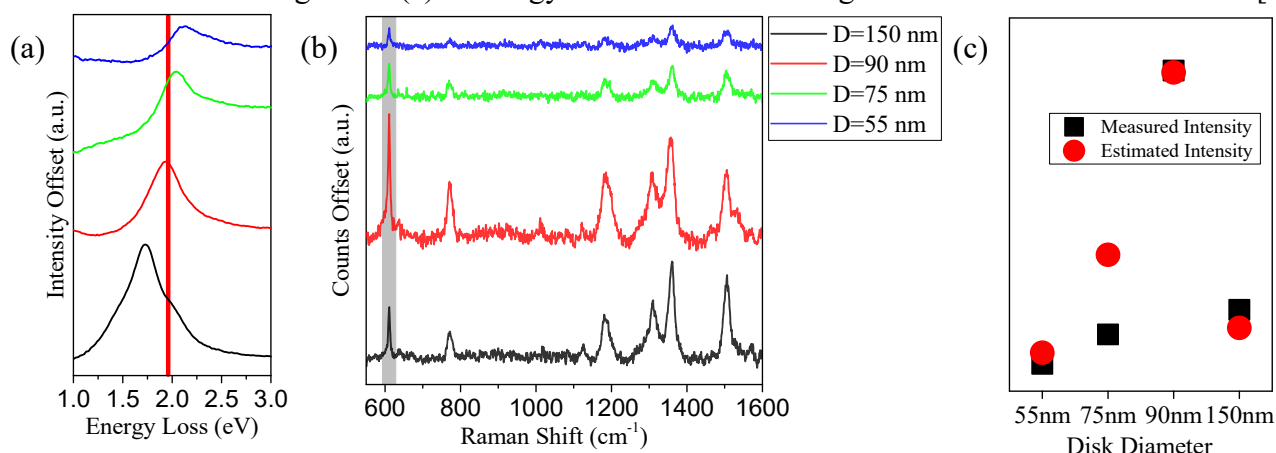


Figure 3. (a) EEL spectra around edges of different size nanodiscs after zero loss peak subtraction showing surface plasmon peaks. The red vertical line represents the 638nm laser energy. (b) Raman spectra measured with 638nm laser. The 90 nm disc array exhibits strongest Raman signal for the 611 cm^{-1} peak. (c) Estimated intensity from EELS based on damped oscillator model and measured Raman integrated peak intensity at 611 cm^{-1} .